NUTRIENT CYCLING IN THE GREAT LAKES:
A SUMMARIZATION OF FACTORS
REGULATING THE CYCLING OF PHOSPHORUS

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INTRODUCTION

The Laurentian Great Lakes of North America contain nearly 20% of the world's lake and river waters and constitute one of the world's largest freshwater resources. Large concentrations of people and industry surround these inland seas. More than one-third of Canada's population and one-eighth of the United States' population lives within the Great Lakes basin. The region accounts for one-fifth of the annual U.S. GNP and one-half of the annual Canadian GNP. Nearly all human activities in the region are associated with the lakes. Those activities include uses for municipal, agricultural, and industrial water supplies; recreation; mining; fishing; and transportation. The Great Lakes also have been used as a convenient disposal site for the wastes of the highly industrial society along the shoreline.

The careless use of the Great Lakes as a disposal site for both toxic and nutrient wastes has diminished the resource value of the lakes, particularly the freshwater fisheries (Smith 1968, 1972). In response to the deteriorating water quality in the Great Lakes, many United States and Canadian agencies have been wrestling with the problem of lake restoration (International Joint Commission 1977). While significant strides have been made in reversing deterioration on a lake-wide basis, it has been recognized that current policies will not likely provide satisfactory improvement in bays and nearshore regions (Thomas et al. 1980). These areas, which are highly impacted by pollution and readily perceived by many people, require additional attention. Subsequent to existing management policies, which are oriented toward relieving background conditions, new policies must address these localized areas.

Cognizant of this requirement and based on the premise that more detailed information is needed to support these second-order policies, the Great Lakes Environmental Research Laboratory is designing long-term research programs to focus on these problems. Prior to design of the research plan, the state of our understanding of the biological, chemical, and physical processes that interact with contaminating substances must be documented.

The purpose of this report is to address the state of our understanding of one aspect of Great Lakes ecosystem function, the cycling of phosphorus. Previous research has identified phosphorus, in particular, as one of the key elements in causing water quality degradation and/or eutrophication in lakes (Dillon and Rigler 1974, Schindler 1978). The rationale for further addressing phosphorus as a polluting substance originates from emphasis on more spatially localized problems, as discussed above. Whereas previous analyses at lake-wide average and annual scales could ignore detailed aspects of internal recycling, present analyses of more localized problems on shorter time scales require improved information on those cycling mechanisms. This report represents the initial step in addressing the research problem on these scales. The information presented below is a review of the state-of-the-art in phosphorus cycling in freshwaters.

The cycling of phosphorus, although of interest ultimately to regulatory agencies, is basically an ecological problem and has been addressed herein through an ecosystem approach. This approach recognizes that essential nutrients affect all components of the aquatic food web both individually and in a composite fashion. The chapters below address each segment of the ecosystem, beginning with chemical species and fractions of phosphorus and moving through bacteria, phytoplankton, zooplankton (herbivores and

carnivores), fish, macrophytes, and benthos. Each chapter is intended to be comprehensive, but not exhaustive. Each chapter is quantitative when possible, although many areas of phosphorus cycling are insufficiently understood for extensive quantification. The movement of phosphorus by predominately physical means has not been addressed in this report, but is considered elsewhere (Lick 1979).

In the final chapter, a framework for understanding the composite movement of phosphorus through the lake ecosystem is presented. This chapter begins with a review of current phosphorus models, and then develops a conceptual model of phosphorus cycling based on a synthesis of available information drawn primarily from the other chapters. The rationale for this model is to place the importance of each component of the food web into perspective in terms of overall phosphorus cycling, and to emphasize those areas where basic information is lacking.

Before the reader begins this report, the intent in preparing this document should be recalled. As mentioned above, this report is intended to be comprehensive, but not exhaustive; it is intended to be factual and informative, but not speculative; and it is intended to serve as a basis for a high quality research program exploring and identifying the major pathways and controls of phosphorus cycling in the nearshore regions of the Great Lakes.

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CHAPTER I

MEASUREMENTS OF PHOSPHATE-PHOSPHORUS IN LAKE WATER

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INTRODUCTION

Reviews on methods for measuring phosphate-phosphorus (PO_4-P) in natural waters have been prepared by Harwood and Hattingh (1973), Kimerle and Rorie (1973), Chamberlain and Shapiro (1973), and Rigler (1973). The purpose of this chapter is to review information on chemical methods for measuring PO_4-P, to describe errors or inconsistencies that can be encountered in performing analyses, and to summarize the importance of interference caused by the hydrolysis of organic compounds or by release of PO_4-P from particles during conventional molybdenum blue analysis. The relationship between bioassay methods for measuring "biologically available P" and analytical PO_4-P measurements is also summarized.

The basic method for estimating PO_4-P concentrations in solution was introduced by Osmond (1887) and applied to analysis of lake-water samples by Denigès (1920) and Atkins (1923). The basic reaction involves complexing PO_4-P with molybdate under acid conditions to form phosphomolybdic acid (a yellow heteropoly acid), which is subsequently reduced by stannous chloride to form a blue complex. The method was improved by Harvey (1948) by adjusting for an optimum ratio of acid normality to molybdate concentration in order to form a stable color and to detect PO_4-P at concentrations approaching 1.0 µg P/L. Since that time, the method has been continuously modified. Olsen (1967), for example, lists over 100 variants of the method that involve alterations in acid normality, molybdate concentration, color development time, and procedures to eliminate interferences or to reduce hydrolytic potentials.

With gradual improvements in analytical techniques and equipment and an understanding of the phosphorus fractions in lake water, the terminology associated with phosphorus analysis has evolved over time (see Olsen 1967). Strickland and Parsons (1965) give the following scheme for the different fractions of P in natural waters (from Rigler 1973):

> Soluble reactive phosphorus (SRP) refers to the value obtained when membrane-filtered water is analyzed by one of the variants of the molybdenum blue technique. This term implies neither that the orthophosphate measured was in solution before addition of the reagents nor that the intensity of the blue color is exclusively a function of orthophosphate concentration rather than that of interfering ions. When "orthophosphate phosphorus" (PO_4-P) is used, it will not refer to the results of chemical analyses but to free orthophosphate in solution, the concentration of which is assumed to be as yet unmeasurable in the trophogenic zone of most lakes.
>
> Soluble phosphorus (SP) refers to the value obtained when membrane-filtered (0.45-µm pore size) water is analyzed after being digested with an oxidizing acid solution.
>
> Soluble unreactive phosphorus (SUP) is the difference between SP and SRP.
>
> Total phosphorus (TP) is obtained by analyzing whole lake water after acid digestion. It is assumed that the values obtained by this technique are indicative of the true phosphorus content of the sample.
>
> Particulate phosphorus (PP) is the total phosphorus minus soluble phosphorus.

As the chemical composition of different phosphorus fractions in lake

water becomes better understood in the future, a more precise and descriptive terminology undoubtedly will evolve. Throughout this and subsequent chapters, the above terminology is used.

TOTAL, PARTICULATE, AND TOTAL SOLUBLE PHOSPHORUS

TP, PP, and SP are determined routinely by digesting samples of lake water and then measuring molybdate-reactive PO_4-P by any one of several molybdenum blue methods (A.P.H.A. 1976, Strickland and Parsons 1972, Golterman and Clymo 1971). Digestion in H_2SO_4, HNO_3, persulfate, or perchloric acid under pressure are common procedures for oxidizing samples. PP normally is estimated by subtracting SP from TP. These digestion procedures, however, are not adequate for some lake waters where highly stable P compounds or minerals containing PO_4-P are present. In such cases perchloric acid, a very strong oxidant, is used in place of acid or persulfate.

METHODS

The basic colorimetric method for SRP analyses involves the addition of ammonium molybdate to an acidified sample (usually 0.1 to 0.4N) to form 12-phosphomolybdic acid which is subsequently reduced (generally with stannous chloride) to form a blue color. After 6 to 12 min is allowed for color development, the optical density of samples and standard solutions of known PO_4-P concentrations are measured (at a wave length near 650 m) in a spectrophotometer. SRP concentrations in samples are obtained from a plot of optical density (corrected for color in reagent blanks) of PO_4-P standards versus known PO_4-P concentrations. Until the mid 1960s, Harvey's technique in one form or another was the time-honored method for measuring SRP.

The ascorbic acid method, developed by Murphy and Riley (1958, 1962), has gained wide-spread popularity within the last 10 years. The method employs ascorbic acid for rapid color development. The principal advantages of the technique are that color development is stable for up to 24 hr or more and all reagents are added from a single "mixed solution," whereas the phosphomolybdate complex formed by Harvey's method is stable only for 20 to 30 min after the reductant is added and acid molybdate and reductant are added individually to samples. Both methods are precise ($\pm$0.10 µg P/L) and have detection limits of ca. 1.0 µg P/L using modern spectrophotometers and cuvettes with a light path of 5 to 10 cm in length. Since SRP concentrations in oligotrophic lakes often are at or below the detection limits of conventional methods, extraction techniques have been developed to increase sensitivity. For example, Stephens (1963) extracted reduced phosphomolybdate by adding reagents of the ascorbic acid method to filtered samples and extracted the reduced complex into isobutanol. Color is stable for 2 hr, the limit of detection is 0.2 µg P/L, and the range is 0.2 to 150 µg P/L. Chamberlain and Shapiro (1969) also developed a method based on extracting phosphomolybdate into isobutanol, which is followed by reduction of the organic extract with stannous chloride. Color development is rapid and stable for a day. The limit of detection is ca. 0.3 µg P/L, and the range is from 0.3 µg to 180 µg P/L.

In the last 15 years, three additional approaches have been used to measure SRP at low concentrations in samples where the long acid exposure times

of conventional methods may overestimate true PO_4-P because of the hydrolysis of P-containing organic compounds or because PO_4-P is released from particles in filtrates. The first method is that of Rigler (1966), who developed a bioassay method where ^{32}P (orthophosphoric acid) and different amounts of reagent PO_4-P are added to samples of lake water. By measuring and plotting the uptake velocity of PO_4-P against the PO_4-P concentrations in samples (assuming different original concentrations of PO_4-P in the water), the maximum value for the true PO_4-P concentration in the sample can be obtained. The method is time-consuming, laborious, and requires specialized equipment, but it is very sensitive and highly reproducible. Comparisons of PO_4-P concentrations measured by radioassay and SRP values determined by conventional methods generally show that SRP is one to two orders of magnitude higher than true PO_4-P concentrations.

The second approach, developed by Crouch and Malmstadt (1967), is based on the fact that as sample acidity is reduced, the rate of color development of reduced phosphomolybdate increases. By lowering acidity and by measuring optical density after a constant time interval, it is possible to perform a sensitive determination before substantial amounts of hydrolysis occur. A similar approach, a 6-sec method, has been developed by Chamberlain and Shapiro (1969). Acid molybdate and reductant are added and color development is measured in 6 sec to circumvent hydrolysis of all but the most labile compounds. This method is highly sensitive and generally gives lower SRP concentrations than conventional methods. The third approach is a new enzymatic technique that currently is in a developmental state (Pettersson 1979). It is based on the ability of PO_4-P to competitively inhibit the hydrolytic activity of alkaline phosphatase from Escherichia coli. Data from Lake Erken, Sweden, show that PO_4-P values measured by the enzymatic method are lower by an order of magnitude than estimates based on conventional analytical methods.

INTERFERENCES

A serious error in most conventional molybdenum blue methods, whether used to measure TP, SP, or SRP, arises from interferences by arsenate or other ions in the same family as PO_4-P. The ions complex with molybdate and are reduced by stannous chloride giving a blue color, which leads to an overestimate of PO_4-P concentrations. This problem is severe in lakes where arsenicals have been used to poison algal blooms or rooted aquatics (see Shapiro 1971). Arsenate interferes in Harvey's method but arsenomolybdate is not extracted into the organic solvent of extraction methods, and it interferes only slightly in the ascorbic acid method when color development time is kept below 12 min. Silica also can interfere in PO_4-P analyses by forming silicomolybdate which is reduced by stannous chloride or other reductants. Silica interference will occur, however, only in the range of pH 3.0-4.0, which is much higher than that of most colorimetric methods where the pH of acidified samples is generally 1.0 or less.

Other types of interferences or errors can arise from "salt effects" or from "hidden blanks." Salt effects are encountered when the rates of color development of reduced phosphomolybdate are different in samples of lake water and in standards prepared in distilled water. PO_4-P concentrations can be underestimated by 20-25% by Harvey's method due to the "salt effect," but the

ascorbic acid method does not appear to be affected appreciably. In all cases, however, it is prudent to use internal standards, i.e. PO_4-P standards prepared in lake water. Serious errors in all colorimetric methods also can arise from the "hidden blank" effect or from the non-specific reduction of molybdate (see Chamberlain and Shapiro 1973). The magnitude of this error, however, is difficult to assess.

HYDROLYSIS AND DESORPTION

One of the principal problems in SRP analyses in natural waters is that dissolved organic compounds or particles <0.50 μm in filtered samples may release PO_4-P under acidic conditions, thus leading to significant overestimates of true PO_4-P concentrations. Despite suspicions and circumstantial evidence for the phenomenon, as well as arguments that hydrolysis does not occur, relatively little research has been done to identify the source(s) of PO_4-P released into solution under the acid conditions of molybdenum blue analyses or to assess the magnitude of the release. Rigler (1966) has shown that colorimetric methods overestimate true PO_4-P concentrations in lake water by 10-100 times, and Kuenzler and Ketchum (1962) and Lean and Nalewajko (1976) showed that the same phenomenon occurs in laboratory algal cultures. Similar results using Rigler's bioassay method have been generated for offshore Lake Michigan water (Tarapchak et al., 1980a) and for an oligotrophic Lake in Ontario, Canada (Levine 1975). The fact that hydrolysis of organic compounds or desorption of PO_4-P from particles occurs during conventional SRP analyses is also supported in theory by the enzymatic method of Pettersson (1979).

The source of the liberated PO_4-P is uncertain, but it has been thought to be from highly labile organic compounds since the "dissolved organic P pool" in lake water is considered to be relatively large (see Rigler 1968). It is unlikely, however, that such compounds are long-lived in the epilimnion of typical north-temperate lakes, where bacteria would quickly degrade them. Chamberlain and Shapiro (1973) also argue against dissolved organic compounds as a significant P source since the average lability of carbohydrate esters expected to occur in lake water is very low.

The most likely source of much of the molybdate reactive PO_4-P pool is from small particles, probably colloids or other particulates <0.45 μm, that pass through membrane filters into filtrates. Evidence for this has come from diverse reports. Tarapchak et al. (1980b) demonstrated that true PO_4-P concentrations could be overestimated by 50-100% using the Chamberlain-Shapiro (1969) extraction technique and that release of PO_4-P from particles <0.45 μm was a significant source. PO_4-P associated with a high molecular weight molecule in water from Lake Tutaeinanga, New Zealand, is liberated by the 6-sec method of Chamberlain and Shapiro (1969), Paerl and Downes (1978), and Schindler et al. (1972) also found that acid molybdate may hydrolyze PO_4-P from relatively large molecular weight colloids reported by Lean (1973a, 1973b) for lake water. Stainton (1980) also has clearly demonstrated that molybdenum blue methods release PO_4-P from colloids in filtered water from a Precambrian Shield lake in Ontario, Canada.

A concerted effort to identify the chemical composition of P-containing particles in lake-water filtrates should be undertaken. Profitable results could be obtained by using techniques such as Sephadex gel filtration, ultra

centrifugation, ion exchange resins, or extraction into different solvents followed by conventional SRP analysis.

FILTRATION ERRORS AND OTHER ARTIFACTS

Serious errors in SRP analyses of lake water can occur when samples are filtered through membrane or other types of filters and from "bottle effects." Dissolved PO_4-P or small particles with adsorbed PO_4-P can be released into filtrates during filtration by leakage from algae or by breakage of other particles, or small P-containing particles that liberate PO_4-P when filtrates are acidified can be trapped in the pores of filters by clogging which excludes them from filtrates (see Rigler 1973). Storage of samples in various types of containers also can lead to increases or decreases in SRP concentrations. Increases can occur if enzymes liberate PO_4-P, and decreases can occur if bacteria attached to the walls of the container assimilate dissolved PO_4-P. In order to minimize these problems, very low vacuum pressures should be used, constant-volume samples should be filtered, and analyses should be performed as quickly as possible after samples are collected and filtered.

BIOLOGICALLY AVAILABLE PHOSPHORUS

As attempts are made to understand more precisely the relationships between phytoplankton growth and phosphorus availability in P-limited lakes, analytical measurements of dissolved PO_4-P have come under close scrutiny. Evidence from some investigations indicates that SRP measurements may not be equivalent to that fraction of dissolved P that is biologically available to phytoplankton and bacteria. Two bioassay techniques have been used: short-term and long-term. Chamberlain and Shapiro (1969, 1973) compared the results of bioassays using P-starved Microcystis aeroginosa (which gave estimates of biologically available P) with estimates of SRP measured by three different analytical methods. After corrections for arsenate interference, the chemical methods gave similar values and they were essentially equivalent to biologically available P. Walton and Lee (1972) also showed in longer-term incubations, where growth instead of nutrient uptake was measured, that SRP measured by the ascorbic acid method agreed with the results of bioassay measurements. In subsequent studies on the biological availability of P in tributaries entering Lake Ontario and in water from Lake Ontario itself, however, Cowen and Lee (1976) showed that on the average biologically available P was equal to the SRP concentration plus 20% of the total phosphorus value of the sample. These results indicate that a significant fraction of the P pool that is not measured as SRP becomes available for phytoplankton growth over time.

These types of results, coupled with the fact that conventional methods measure SRP rather than truly dissolved PO_4-P (see Rigler 1966 and others above), are paradoxical. Since algae take up truly dissolved PO_4-P (Kuhl 1974), and colorimetric methods overestimate this fraction of the dissolved P pool in lake water (Rigler 1966), how do algae take up SRP that is not present as truly dissolved PO_4-P in lake water? The most logical explanation for this phenomenon is that algae do assimilate only truly dissolved PO_4-P and that much of the SRP is made available to the algae by one or both of two mechanisms:

(1) an inducible enzyme, alkaline phosphatase, synthesized by P-starved algae, liberates PO_4-P from dissolved organic compounds (see Berman 1970), or (2) when the concentration of truly dissolved PO_4-P is depleted by algal uptake, the equilibrium between the dissolved and the particulate PO_4-P pool in lake water shifts, releasing PO_4-P from particles into solution. Further research is necessary to identify the chemical forms of P compounds and complexes in the SRP pool that are biologically available and how rapidly they are produced and taken up by algae. Information on the cycling rates of different chemical fractions of P in lake water and factors that may affect their biological availability are presented in the next chapter.

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CHAPTER II

CHEMICAL FACTORS CONTROLLING PHOSPHORUS CYCLING IN LAKES

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INTRODUCTION

Phosphorus is a principal nutrient limiting primary production in most fresh waters including the Great Lakes (PLUARG 1978). Phosphorus enters lake systems through tributaries and land runoff (Schaffner and Oglesby 1978, Gakstatter and Allum 1978), direct discharge from human activities (Heidtke et al. 1979), and atmospheric sources (Eisenreich et al. 1977, DeLumyea and Petel 1977). An estimate of total phosphorus loads to the Great Lakes is provided in Table 1 (Chapra and Sonzogni 1979). Diffuse tributary input, resulting in large part from agricultural land runoff, accounts for a large portion of total phosphorus added to the Great Lakes (Chapra and Sonzogni 1979). The effect of phosphorus added to or regenerated in a lake depends not only on the total quantity of phosphorus in the water but also on chemical form, availability, and residence time in the water. These factors are initially a function of the phosphorus source but ultimately are controlled by in situ processes.

Phosphorus chemistry in lakes is simplified by the fact that the element exists in nature almost completely in the oxidized form as phosphate (Stumm and Morgan 1970, Williams 1978). However, other factors, including the strong tendency of phosphate to sorb to and be released from particulate materials, complicate understanding of phosphorus cycling in aquatic systems. Phosphorus in lakes can be categorized according to chemical form or classified by size into dissolved, particulate, and colloidal components. Chemical data on phosphorus cycling in the Great Lakes have been collated and summarized by Torrey (1976) and Upchurch (1976). Laboratory studies and field observations have provided insight into the chemistry and biological availability of different phosphorus forms in natural waters, but exact mechanisms and rates of many reactions affecting phosphorus cycling are not known (Torrey 1976). This chapter will emphasize aspects of phosphorus chemistry which affect nutrient cycling in the Great Lakes. An attempt will be made to briefly describe known concepts and indicate areas where future research is needed.

CHEMICAL FORMS OF PHOSPHORUS

Phosphorus in aquatic ecosystems occurs as phosphate in organic and inorganic compounds. Free orthophosphate is the only form of phosphorus believed to be utilized directly by phytoplankton (Rigler 1973) and thus represents a major link between organic and inorganic phosphorus cycling in lakes. In natural waters, orthophosphate occurs in ionic equilibrium, i.e.

$$\text{as } H_3PO_4 \overset{pK = 2.2}{\longleftrightarrow} H_2PO_4^- \overset{pK = 7.2}{\longleftrightarrow} HPO_4^{2-} \overset{pK = 12.3}{\longleftrightarrow} PO_4^{3-}$$

with $H_2PO_4^-$ and HPO_4^{2-} being the predominant species over pH range of 5 to 9 (Stumm and Morgan 1970). Figure 1 approximates the inorganic species distribution over pH ranges which occur in the Great Lakes. Complexation of phosphorus by major ions is significant in sea water; only 56 percent of the HPO_4^{2-} and 0.4 percent of the PO_4^{3-} are estimated to be in free ionic form

TABLE 1. Annual total phosphorus loads (metric tons per year) to the Great Lakes for the mid-1970s (taken from Chapra and Sonzogni 1979).

	Point direct	Point tributary	Diffuse tributary[a]	Atmospheric	Total Loading[b]	Shoreline erosion
Lake Superior	300	200	2,400	1,100	4,000	3,800
U.S.	150	150	1,000 (750-1,200)			3,800
Canada	150	50	1,400 (1,100-1,900)			Minimal
Lake Michigan	1,850	1,400	2,000 (1,400-2,000)	1,700	6,950	3,700
Lower Green Bay	450	300	400	50	1,200	Minimal
Upper Green Bay	Minimal	Minimal	150	50	200	100
Main lake	1,400	1,100	1,450	1,600	5,500	3,600
Lake Huron	250	725	2,500	1,100	4,575[5,472][c]	700
U.S.	100	550	1,200 (700-1,100)			300
Canada	150	175	1,300 (900-1,400)			400
Georgian Bay	50	25	500	300	875	Minimal
Saginaw Bay	50	550	800	25	1,425	25
Main lake	50	150	1,200	775	2,275	675
U.S.	50	Minimal	400			275
Canada	100	150	800			400
Lake Erie	7,000	1,350	9,000	800	18,150[19,047][c]	10,450
U.S.	6,000	1,150	6,700 (3,700-7,000)			1,000
Canada	250	200	2,300 (1,300-2,700)			9,450
Western basin	5,950	650	4,400	100	11,100	250
U.S.	5,700	550	3,900			150
Canada	250	100	500			100
Central basin	900	500	2,700	500	4,600	9,200
U.S.	900	500	2,200			450
Canada	Minimal	Minimal	500			8,750
Eastern basin	150	200	1,900	200	2,450	1,000
U.S.	150	100	600			400
Canada	Minimal	100	1,300			600
Lake Ontario	2,250	1,150	2,800	450	6,650[10,444][c]	1,300
U.S.	1,100	1,000	1,700 (800-1,400)			500
Canada	1,150	150	1,100 (700-1,400)			800

[a] Range in parentheses is an estimate of the likely range in diffuse tributary loading due to year to year flow variations. [b] Excluding shoreline erosion. [c] Number in brackets includes input from upstream lakes.

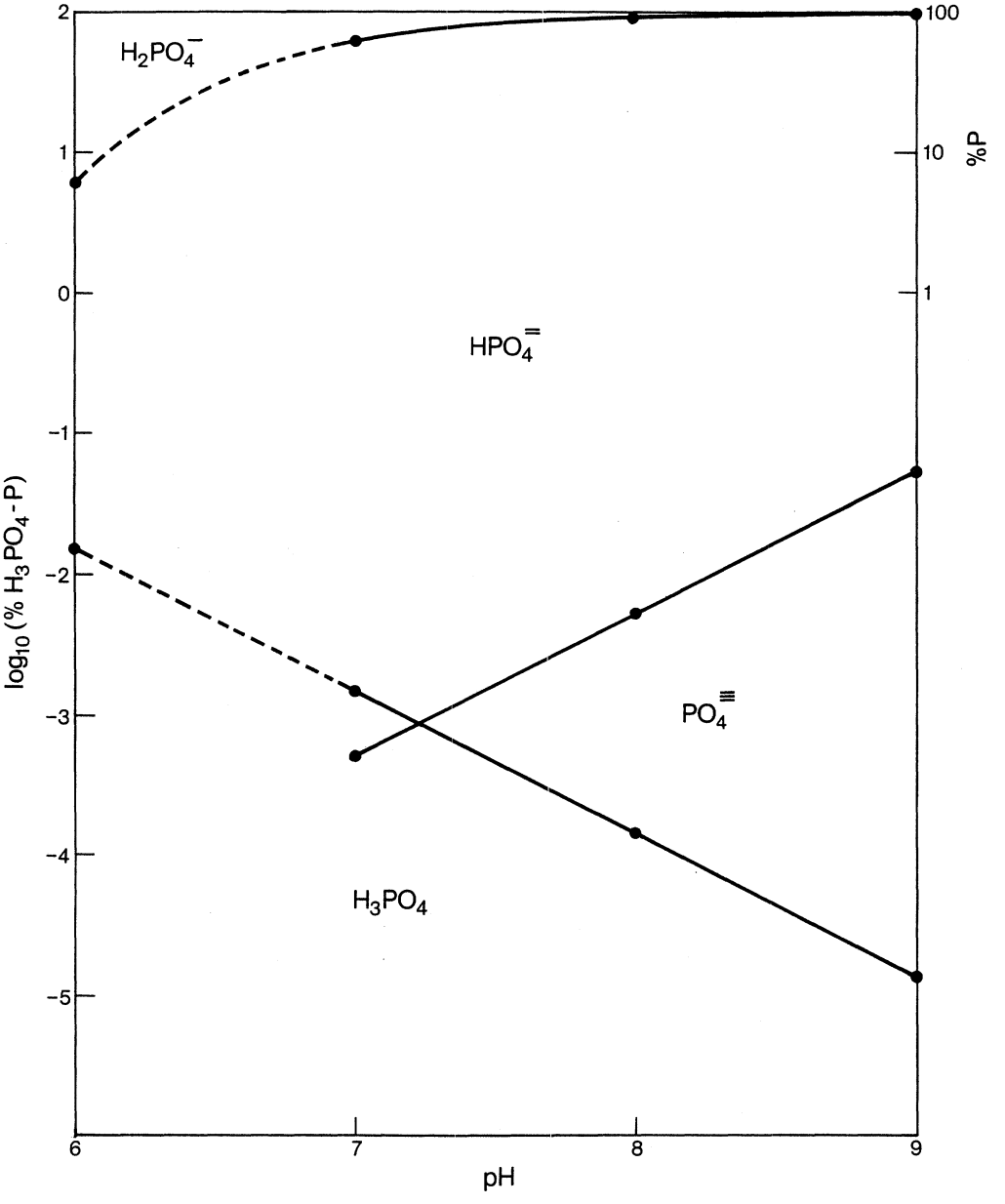

Fig. 1. Species distribution of H_3PO_4 in distilled water (25°C). Data from Gulbransen and Roberson (1973). Complexation in natural waters alters distribution.

(Kester and Pytkowicz 1967). Ca^{2+} is the dominant complexing ion in ocean water (Chughtai et al. 1968). Although calcium concentrations are lower by an order of magnitude in Great Lakes water than in sea water, calcium is the major cation in the Great Lakes and may complex with dissolved phosphorus.

Dissolved inorganic phosphorus also occurs as condensed phosphates which originate from biochemical phosphorus compounds (e.g. ATP; Holm-Hansen 1969) or may be derived from detergents in waste waters (Heinke 1969). In addition to soluble forms, inorganic phosphates may be incorporated into minerals or can be sorbed to lake sediments (Hwang et al. 1976, Williams et al. 1980), particulate organic material (Williams et al. 1958), clay particles (McCallister and Logan 1978), or inorganic precipitates such as metal hydroxides or oxides or $CaCO_3$ (McCallister and Logan 1978, White and Wetzel 1975).

Phosphorus occurs in organisms as orthophosphates, phospholipids, nucleic acids, nucleoproteins, coenzymes, and phosphorylated sugars (Alexander 1961). Phosphate is sometimes accumulated by phytoplankton in excess of their metabolic needs as "luxury uptake" (Reynolds 1978; Lehman, Chapter IV).

In addition to being a cellular component of organisms, organic phosphorus occurs in natural waters as dissolved organic forms or as non-living particulate organic compounds. These non-living fractions include residues of plants, animals, or microbes, and diagenetic breakdown products of these residues. Although organic phosphorus compounds originate from incorporation of phosphate into living material, organic components of aquatic systems may contain organic phosphates in forms considerably modified from that present in living material (e.g. humic substances, Nissenbaum 1979). Readily degradable (labile) organic phosphorus compounds by definition do not exist for long periods in the water after being released from organisms by excretion or death. Some organic phosphorus compounds formed by plants and other organisms appear relatively resistant to decomposition. For example, phytic acid (inositol hexaphosphate) has been found to be resistant to decomposition in natural water (Rodel et al. 1977). Other compounds (nucleotides and sodium glycerophosphate) have intermediate stability and decompose over a period of weeks in laboratory experiments (Rodel et al. 1977).

Of all phosphorus components in natural waters and sediments, the non-living organic fractions are probably the least understood and may be chemically the most complex. A primary reason for this lack of understanding is the absence of suitable standard methodology to isolate and measure component compounds. Most analytical schemes commonly used for phosphorus measurements in natural waters quantify organic compounds by difference rather than by direct measurement of component compounds (Strickland and Parsons 1972, Standard Methods 1976). To achieve a comprehensive picture of organic phosphorus composition and activity in lakes, specific compounds or groups of compounds should be isolated and measured. Methods recently developed for specific groups of compounds have been used to verify the presence of inositol phosphates (Weimer and Armstrong 1977, Eisenreich and Armstrong 1977, Herbes et al. 1974), nucleic acids (Minear 1972), and ATP (Riemann 1979), but the composition of a large fraction of dissolved and particulate organic phosphorus materials remains unidentified (Nissenbaum 1979).

Division of organic material into dissolved and particulate fractions is generally done by filtration (Standard Methods 1976). Materials passing through a 0.45 micron pore size filter are arbitrarily labeled as dissolved and those retained by the filter as particulate. A third category, the colloidal fraction, cannot be strictly termed as dissolved or particulate but can logically be considered as a third independent component. Colloidal material

constitutes a large fraction of organic material in lake water (Allen 1976) and may be relevant to phosphorus since much dissolved phosphorus in natural waters is associated with high molecular weight organic material (Downes and Paerl 1978).

Categorizing phosphorus on the basis of solubility or other operationally defined characteristics may be misleading because phosphates can rapidly exchange between different aquatic compartments (Rigler 1956). Isotopic studies in conjunction with molecular size fractionations have been used to define interactions between orthophosphate, particulate phosphorus, and dissolved organic phosphorus in lake water. For example, phytoplankton have been shown to release low molecular weight (ca 250) organic phosphorus compounds which subsequently combine into high molecular weight colloids with partial loss of orthophosphate back into solution (Lean 1973). Orthophosphate can be released from organic phosphorus compounds in water by enzymes (e.g. phosphatases) or from colloidal humic material by low doses of ultraviolet light (Franco and Heath 1979).

CHEMICAL REACTIONS AFFECTING PHOSPHORUS CYCLING

Reactions that can affect phosphorus cycling in lake water and sediments include precipitation (and floculation), complexation, redox reactions, sorption, acid-base, and a variety of biochemical reactions (Lee and Hoadley 1967). These reactions are in turn affected to varying degrees by factors such as pH, Eh, temperature, and light. Thermodynamic considerations allow prediction of forms and relative concentrations of inorganic phosphorus under equilibrium conditions when Eh and pH conditions and chemical composition are known. Potential roles of precipitation, complexation, and redox reactions and maximum levels of inorganic components can be predicted thermodynamically using solubility or complexation products when chemical conditions of a parcel of water are defined (Stumm and Morgan 1970). Equilibrium models such as WATEQ (Truesdell and Jones 1973) can be used to estimate thermodynamic inorganic phosphate partitioning with major cations and anions in the Great Lakes under various winter and summer conditions (Table 2). In this model, HPO_4^{2-} is the major form of inorganic phosphorus in the water followed in importance by calcium and magnesium complexes of phosphorus.

Thermodynamic calculations based on laboratory observations should be extrapolated to lake waters only with caution because of the many complex features which make lake systems different from conditions in the laboratory. A major factor complicating phosphorus chemistry in lakes is the presence of organisms which dramatically affect nutrient cycling and limit the usefulness of thermodynamic calculations to predict composition and concentrations of nutrient forms (Lee and Hoadley 1967).

Complexation and Precipitation Reactions

As mentioned above, phosphate ions can form soluble complexes or insoluble precipitates with cations, such as Fe, Ca, Mg, and Al, if concentrations of the metals and phosphates are sufficiently high. Formation of soluble phosphate complexes in lake water may not affect availability of soluble phosphorus to organisms but may prevent precipitation or sorption of phosphates when

TABLE 2. Equilibrium distribution of phosphorus species.

	Lake Michigan		Lake Ontario		Lake Superior
	Summer	Winter	Summer	Winter	Winter
Input					
Temp °C	20	2	20	2	2
pH	8.5	8.5	8.5	8.1	8.1
Ca mg/l	34.	34.	42.	42.	12.9
Mg	11	11.	8.	8.	2.7
Na	5	5.	13.5	13.5	1.3
K	1.1	1.1	1.4	1.4	0.5
Cl	7.0	7.0	30	30.	1.2
SO4	16	16.	29	29.	2.3
HCO_3	128.7	128.7	114.	114.0	51.4
SiO_2	1.0	1.0	0.3	0.3	3.0
Fe	0.01	0.01	0.05	0.05	0.1
PO_4	0.01	0.01	0.01	0.01	0.001
Output	As % of inorganic P				
$FeHPO_4^+$					
$FeHPO_4$			0.01	0.05	0.13
FeH_2PO4^+					
FeH_2PO4^{++}					
PO_4	0.01	0.008	0.11	0.03	0.003
$HPO4^=$	58.	66.7	57.8	67.1	75.6
H_2PO^{4-}	2.4	3.0	2.4	8.6	9.3
$MgPO_4^-$	7.0	3.9	4.9	1.2	0.6
$MgHPO_4$	9.4	7.9	7.0	6.1	2.8
$MgH_2PO_4^-$	0.02	0.01	0.01	0.04	
$CaPO_4$	9.4	6.0	11.9	2.8	1.1
$CaHPO_4$	13.3	11.2	16.1	14.1	6.1
$CaH2PO_4^+$	0.04	0.04	0.04	0.10	4.4
$KHPO_4^0$					
$NaHPO_4$	0.02	0.02	0.07	0.08	

phosphorus levels are high. Under conditions of sufficient phosphate and calcium levels and high pH, calcite may be converted to hydroxyapetite (Stumm and Morgan 1970). A review of solubility products and expected levels of phosphates and metals in sediment waters led Syers et al. (1973) to conclude that metal precipitates of phosphorus [$ALPO_4$ (variscite), $FePO_4$ (strengite), and $Ca_{10}(PO_4)_6(OH)_2$ (hydroxyapatite)] are not important for removing phosphate from sediment water solution. An exception may be hydroxyapetite in some lakes, but amounts of this precipitate in lake sediments are low (<5% of inorganic phosphorus; Schofield 1968) and do not appear to be quantitatively important (Syers et al. 1973).

Sorption, Redox, and Acid-base Reactions

Phosphates are strongly sorbed by a variety of particulate materials including clays, organic particulates, and various precipitates of metals. Examples of the latter are the common use of $CaCO_3$ and alumina to remove phosphorus from waste water in treatment plants. Phosphorus does not participate directly in redox reactions under most environmental conditions but can be sorbed by precipitates which form as a result of redox conditions. In natural waters containing Fe, Mn, or Al, orthophosphate is sorbed to the oxide and/or hydroxide gels of these metals (which form under oxygenated conditions) but is released when the precipitates dissolve under reducing conditions (Syers et al. 1973). Removal of phosphate from solution by this mechanism in oxygenated waters and release of phosphorus back into reduced waters is a well-known phenomenon in lakes and may be the most important chemical phenomenon affecting phosphorus distribution and cycling in aquatic systems. The quantity of phosphorus sorbed to metal precipitates can be reduced by organic anions which chelate the metals (Earl et al. 1979).

Humic substances in sediments can bind phosphates from overlying lake waters. Nutrients added to hypolimnetic waters of a small Canadian experimental lake caused minimal eutrophication effects, relative to effects caused by addition of nutrients to surface waters of a similar lake (Schindler et al. 1980). Phosphorus added to the hypolimnion was transferred efficiently to colloidal material in the sediments with no detectable return to overlying waters. Phosphorus dynamics in the Great Lakes may be different, however, because Great Lakes sediments likely contain less humic material and have higher redox potentials than do the experimental lakes. Great Lakes waters are subject to large scale physical processes (Boyce 1974) which may result in more nutrient exchange than occurs in the Canadian experimental lakes.

Three of the Great Lakes (Michigan, Erie, and Ontario) undergo a seasonal epilimnetic autogenic precipitation of $CaCO_3$ (Strong and Eadie 1978). These particles are postulated to serve as efficient substrates for phosphorus sorption. Their large size (ca 10 μm) and dense structure cause them to sink rapidly and remove phosphorus from euphotic zones. After reaching the hypolimnion the particles in part dissolve and thereby release transported phosphorus back into solution (unpublished data).

Phosphorus can attach to clays by chemically bonding to the positively charged edges of the clay particles or by substituting phosphates for silicates in the clay structures. Phosphates most effectively sorb to clays at pH's of less than neutral (Stumm and Morgan 1970). Since clays do not normally dissolve under reducing conditions, sorption to clays presumably is less

dependent on Eh conditions than is sorption to oxidized metal precipitates. Organic phosphates (e.g. nucleotides, nucleic acids, nucleoproteins, inositol phosphates, and glycerophosphates) are sorbed by clays and other particles (e.g. Goring and Bartholomew 1952, Anderson and Arlidge 1962). Sorption of inositol phosphates by clays is greatest at pH 3 to 4 and increases with the number of phosphates in the organic molecule (Anderson and Arlidge 1962). Since phosphate esters are sorbed through phosphate groups, sorption of organic phosphorus compounds can be expected to resemble that of inorganic phosphate (Syers et al. 1973). In addition, organic phosphorus compounds may be sorbed to hydrophobic organic portions of particles.

Acid-base reactions relate directly to pH which controls the relative concentrations of orthophosphate forms in solution (under equilibrium conditions) and may indirectly affect phosphorus chemistry and cycling by influencing sorption, precipitation, complexation, redox, and biochemical reactions (e.g. Lee and Hoadley 1967).

Biochemical Reactions

Due to its nutritive importance in lake ecosystems, available phosphorus is rapidly removed from solution by phytoplankton in photosynthetic zones (Rigler 1973). This mechanism reduces (and maintains) the amount of dissolved orthophosphate in the epilimnion during summer stratification to levels lower than normally measured by standard analytical techniques ($<1\ \mu g\ L^{-1}$, Rigler 1973, Paerl and Downes 1978). Other organisms exert major effects on phosphorus cycling by immobilizing phosphorus, by making non-orthophosphate forms available to phytoplankton, or by phosphorus uptake. Interactions of phosphorus with aquatic organisms and mechanisms affecting its availability will be discussed in later sections.

Sediment Phosphorus Chemistry

Sediments are important "buffering mediums" which can influence phosphorus levels in lake waters (Kuo and Lotse 1974). Since photosynthesis is absent (except possibly at sediment surfaces), biological processes result in a net mineralization rather than production of organic matter in sediments. Modified redox potentials and high concentrations of inorganic ions and of sediment particles, relative to lake water, make the sediment environment potentially conducive to many reactions discussed above and make sediments an important potential source of nutrients to lakes.

Factors affecting exchange rates of phosphates and other nutrients across sediment-water interfaces include physical turbulence, redox potential, temperature, pH, relative concentration gradients, biological activity, cation distribution, and sediment composition (Kamp-Nielsen 1974, Holdren and Armstrong 1980). In many lake sediments, phosphorus is associated with iron, and levels of the two elements are directly correlated (Syers et al. 1973). The major factor controlling phosphate exchange in anaerobic sediments is the phosphate concentration gradient (across the sediment-water interface) which is controlled by pH and redox potential of the sediments (Kamp-Nielson 1974). Except for the central basin of Lake Erie and polluted bays and harbors, sediment-water interfaces in the Great Lakes are generally not in a reduced

state (Mortimer 1971). Therefore, the mechanism and extent of phosphorus exchange of oxygenated sediment layers with the overlying water is of particular interest for these waters.

Exact mechanisms of phosphorus exchange between lake sediments and water have not been completely defined but involve several interactive processes. Actual levels of phosphate or other nutrients measured in hypolimnetic or pore waters do not provide complete information on their flux to and from sediments because addition and removal processes may occur simultaneously and result in a small net concentration in the water. ^{32}P tracer studies have been used to graphically portray phosphorus exchange between sediment and water as two (Pomeroy et al. 1965) or more (Li et al. 1972) first order reactions. Laboratory and field studies have shown that phosphorus sorption and release by sediments is affected by time of exposure (Kuo and Lotse 1974, Hwang et al. 1976), phosphate concentration and sediment particle size (Hwang et al. 1976), redox, temperature, mixing intensity, and bioturbation (Holdren and Armstrong 1980). Freshly adsorbed phosphorus is much more "exchangeable" than native phosphorus in sediments (Kuo and Lotse 1974). Likewise, phosphates recently sorbed to particulate materials entering the Great Lakes have more potential biological significance than phosphorus incorporated into minerals or other refractory particles.

PHOSPHORUS AVAILABILITY TO AQUATIC PLANTS

To understand the impact of phosphorus (from external or internal sources) on a lake ecosystem, availability of component phosphorus compounds to aquatic plants must be understood. Any form of phosphorus present in (or added to) a lake can be categorized as being immediately available, potentially available, or likely unavailable. The principal form of phosphorus known to be directly available to plants is orthophosphate (Hooper 1973). Potentially available phosphorus forms include a large number of compounds which can be converted to orthophosphate and thus become available to phytoplankton. This category includes inorganic condensed phosphates, biochemical forms of phosphorus, and other sorbed or complexed forms of phosphorus in the water. Phosphates chemically incorporated into high molecular weight compounds are partially available to algae (Paerl and Downes 1978). Potentially available phosphorus can appropriately be further categorized into forms available over short periods (hours-days) and forms which become available over long periods (weeks-months).

The likely unavailable phosphorus compounds are relatively abundant in lakes but are probably the least understood of the above categories (Nissenbaum 1979). A logical explanation for their abundance is that they are the residual compounds left after more labile compounds are removed from the water or particulate material. Although very few forms of phosphorus in the environment can be considered as totally unavailable over long periods (years), some forms (e.g. apetite and other minerals) are likely unavailable during their residence in lakes (Williams et al. 1980, Lee et al. 1980). More than half the phosphorus contributed to the Great Lakes by tributaries has been estimated to be unavailable for plant growth (Chapra and Sonzogni 1979). Rates of availability and particle residence times in the water must both be considered to correctly estimate potential biological use of particulate phosphorus added to lakes (Verhoff and Heffner 1979).

Availability of organic phosphorus is not well understood for particulate or dissolved forms. At least a portion of reactive phosphorus in high molecular weight organic compounds in lakes can be made available for algal uptake, but the time required for utilization is longer than for orthophosphate (Paerl and Downes 1978). Enzyme activity may be responsible for making organic phosphorus available to phytoplankton (Herbes et al. 1974, Paerl and Downes 1978).

Chemical Techniques to Estimate Bioavailability

Various methods to evaluate or estimate availability of particulate phosphorus to aquatic plants have been recently reviewed (Armstrong et al. 1979, Logan et al. 1979, Williams et al. 1980, Lee et al. 1980). Algal assays (based on increased algal biomass resulting from particulate phosphorus utilization) have been developed and standardized (USEPA 1971, 1974). These methods are effective for estimating short-term potential availability but do not provide complete information on actual availability in lakes. Some particulate material may be removed from the euphotic zone before potentially available phosphorus is released (Williams et al. 1980). Other material may degrade slowly (e.g. some organic phosphates) or may remain suspended in the water for a long period (e.g. clay-sized particles) and may ultimately be more available than predicted (Armstrong et al. 1979, Lee et al. 1980).

Chemical extraction techniques using dilute acid, base, or complexation solutions or ion exchange resins have been used to approximate biological availability (Cowen and Lee 1976, Armstrong et al. 1979, Logan et al. 1979, Williams et al. 1980). Chemical methods to assess phosphorus availability must, of necessity, be empirical. One scheme (Allen and Williams 1978) defines non-apetite phosphorus as that extracted by citrate-dithionte bicarbonate and apetite phosphorus as that extracted from sediments with dilute acid (HCL or H_2SO_4). Dilute acid removes more phosphorus from particulate material than do algae (Selanastrium capricornutum), presumably because it extracts unavailable phosphorus from apetite and other minerals. Base and anion exchange extractions of particulate material agree more closely with bioassays than do acid extractions (Cowen and Lee 1976). It has been proposed that anion exchange extraction removes phosphorus which is readily available to organisms, whereas the NaOH extraction is a better indicator of the maximum amount of inorganic phosphate which could be made available if phosphorus is removed from solution (Armstrong et al. 1979). Other workers (Logan et al. 1979) consider phosphorus extracted by NaOH to represent short-term availability and the total quantity of phosphorus sequentially extracted by NaOH and citrate-dithionate bicarbonate to represent the total phosphorus available. Based on comparison of chemical studies with bioassay results (Cowen and Lee 1976), available phosphate was estimated to be roughly equal to soluble reactive phosphorus plus 20 percent of total particulate phosphorus for Great Lakes tributary waters (Lee et al. 1980). Selanastrium capricornutum bioassays on sedimentary materials from Lakes Ontario and Erie, tributaries, and eroding bluffs indicated that available phosphorus cannot be estimated accurately by measuring total phosphorus but is directly related to quantities of inorganic non-apetite phosphorus in the particulate matter (Williams et al. 1980). Rate of availability of total phosphorus in Lake Erie tributary water has been examined by measuring biological (algal) accumulation of phosphorus from test waters with time over extended (60-80 days) periods (Verhoff and Heffner 1979).

Processes Making Phosphorus Available to Aquatic Plants

Phosphorus is made available by processes that convert non-available forms to orthophosphate or that transport phosphate from unlighted regions into photosynthetic zones of lakes. Sediments are known sinks for phosphorus (Mortimer 1941) and are a major reservoir of phosphates which can potentially be made available to organisms through chemical, biological, and physical processes. Particulate material can release phosphorus while settling through the water column and after reaching the sediments. If water and/or sediments are oxygenated and sufficient iron is present, a ferric hydroxide gel forms and sorbs dissolved phosphate from solution and thereby prevents (or hinders) phosphate from becoming available to organisms in the photosynthetic zone (Syers et al. 1973).

Although it is commonly assumed that oxygenated sediments are strictly a phosphorus sink, some studies (e.g. Lee et al. 1977) suggest that phosphates can be released from oxygenated sediments. Although the rates of release are slower than for reduced sediments, phosphorus contributions from oxygenated sediments can potentially be substantial and should be considered in comprehensive models of phosphorus dynamics. Processes that can make phosphorus available from sediments include biological, chemical, and physical phenomena. Biological regeneration of phosphates from sediments by benthic macro-organisms and microbes appears to be an important mechanism to return particulate phosphorus to water in dissolved form and is discussed in Chapter VI. Chemical changes in redox potential cause phosphates to be released when metal precipitates dissolve causing increased phosphate levels in pore water and in hypolimnetic waters. Physical mixing of the upper layers of the sediments results in transport of phosphorus-rich pore water with hypolimnetic water to photosynthetic zones. Sediment material containing exchangeable phosphorus may also be mixed with bottom water to form a nepheloid layer (Chambers and Eadie 1980) which can be a mode of phosphate transport when transported to photosynthetic zones. Availability of nepheloid phosphorus should be studied in detail; preliminary results by the NaOH extraction technique from southeastern Lake Michigan indicate that 20-50% of the total P in the nepheloid layer becomes available. Quantitatively this is approximately equal to the total phosphorus pool in the water column (Eadie, B. J., unpublished data). After phosphorus is transferred from sediments into hypolimnetic waters, other physical processes (spring overturn, bottom current movement, and wind-induced upwelling events) can move potentially available phosphorus into photosynthetic zones (e.g. Mortimer 1969, Stauffer and Lee 1973). These processes should be thoroughly studied to enhance understanding of Great Lakes nutrient dynamics.

Modeling studies (Scavia 1979) and other work (cf. Hooper 1973) have suggested that much of the utilized phosphorus in lakes is made available to phytoplankton through regeneration processes. It can be reasonably hypothesized that much of the phosphorus is rapidly returned to the orthophosphate (or other available) form through excretion or death of aquatic organisms. Biochemical processes are likely primarily responsible for converting organism-derived phosphorus compounds back to orthophosphate. Zooplankton release orthophosphate as part of their normal metabolism (Marshall

and Orr 1955, Rigler 1961, Pomeroy et al. 1963, Barlow and Bishop 1965). Autolytic enzymes may convert organic forms of phosphorus to orthophosphate when organisms die. High energy forms of phosphate in living organisms (e.g. ATP) are not stable for long periods (minutes) after the organism dies (Christian et al. 1975). Phytoplankton produce extracellular enzymes (phosphatases) which can free orthophosphate from organic phosphorus compounds (Paerl and Downes 1978). Stability of dissolved organic compounds to enzymatic decomposition could be a major factor regulating levels of organic phosphorus in lake water.

Factors Making Phosphorus Unavailable to Organisms

Available phosphorus in lake systems can be converted into forms which are unavailable to phytoplankton by 1) physical-chemical processes which remove phosphorus from solution and/or transfer it from photosynthetic zones and 2) biological processes which convert utilized phosphorus into refractory (unavailable) dissolved or particulate forms. Particulate material which does not degrade will ultimately be transported into the sediments by settling, or out of the lake with outflowing water. Refractory phosphorus in dissolved or colloidal organic compounds may become incorporated into particulate material by forming aggregates or by sorbing to particulates such as clays, inorganic precipitates, or organic particles. Remaining dissolved refractory material will move with the water conservatively. The relative quantity of organic phosphorus in lakes which is refractory over the time scale of months or seasons is not known, primarily because the composition and relative stability of component compounds are not known. Also unknown are the relative functions of plants, animals, and microbes in forming refractory compounds (Hooper 1973). If turnover is not rapid for some organic materials, phosphorus in these substances would be measured in the non-living fraction but could become available later for phytoplankton use. Substances which are rapidly decomposed would not be present in measurable quantities except for catastrophic occasions (e.g. death of an algae bloom; Gardner and Lee 1975) which add large amounts of these compounds over short time periods. Organic forms of phosphorus thought to be at least partially unavailable over long (<months) periods include some inositol phosphates (e.g. phytic acid; Eisenreich and Armstrong 1977) and high molecular weight humic materials (Nissenbaum 1979). Speciation of phosphorus components of humic and fulvic materials in lakes and their ability to exchange phosphorus have not been carefully investigated (Nissenbaum 1979).

SUMMARY AND RECOMMENDATIONS

Summary

The importance of component phosphorus compounds to a phosphorus-limited lake system is determined by their concentration, chemical form, availability to organisms, and residence time in photosynthetic zones. Phosphorous occurs (as phosphate) in dissolved, particulate, and colloidal components of lake ecosystems. Dissolved forms include orthophosphate, condensed inorganic phosphates, and dissolved organic phosphates. Particulate material can arbitrarily be divided into living and non-living forms containing 1) naturally

incorporated phosphates and 2) sorbed and/or loosely bound phosphates. Colloidal inorganic or organic phosphates may be important to phosphorus cycling in lakes, but are not well defined. Organic phosphates in lake water include inositol phosphates, nucleic acids, nucleotides, and humic materials; the composition of other organic phosphorus components is unclear. Since orthophosphate is the only form known to be available to plants, other forms of phosphorus presumably must be converted to orthophosphate to affect biological dynamics.

Phosphate levels in lakes can be affected directly by complexation and precipitation reactions, but sorption and biochemical reactions appear to be the most important chemical factors controlling phosphorus dynamics. Phosphorus does not normally undergo redox changes in nature, but its form and concentration in water are often controlled by sorption to (or release from) colloidal or particulate metal hydroxides which form or dissolve as a function of redox potential. Phosphorus is thus removed from solution under oxygenated conditions and dissolved into solution under reduced conditions. Clay particles, $CaCO_3$ precipitates, and colloidal or particulate organic materials affect lake water phosphorus levels by sorption and desorption.

During summer stratification, biological uptake by phytoplankton is a primary factor controlling orthophosphate levels in phosphorus-limited euphotic zones. Biochemically accumulated phosphate is returned to the water by excretion (by zooplankton and other animals), autolytic release after death of organisms, and (possibly) as a result of degradation of non-living organic materials. Biochemical reactions which result in the formation of phosphorus compounds resistant to decomposition are potential mechanisms for making phosphorus unavailable in lake water. The availability of phosphorus in nonliving organic dissolved and particulate material is not well known, in part because the composition of phosphorous-containing organic material in lake water has not been well defined. Biological methods (based on growth of algae in phosphorus-limited cultures) and chemical extraction methods, which have been empirically correlated with algal growth, have been used to estimate availability of phosphates associated with particulate materials.

Sediments are important sinks for phosphorus in lake systems, but can also be a source of orthophosphate to photosynthetic zones if chemical, biological, and physical conditions liberate orthophosphate (or other available phosphorus compounds) and transfer it to the epilimnion. Phosphorus chemistry in sediments and lower hypolimnetic waters differs from that in surface waters because concentrations of chemicals and particulate materials are higher and redox potentials are generally lower in these regions than in epilimnetic zones.

Recommendations

Processes controlling internal phosphorous cycling must be clarified and quantified to properly determine effects of changing the levels and/or compositions of phosphorus from external sources. A comprehensive understanding of phosphorus aquatic chemistry in lakes is needed to accurately predict biological effects of added phosphorus. To understand phosphorus dynamics in the Great Lakes, the composition and cycling rates of major component compounds must be defined. Specific compounds or groups containing phosphorus should be identified and their stability and flux rates should be determined. Quantity, composition, and potential availability of phosphorus

compounds entering the lakes from aquatic and atmospheric sources should be evaluated, so that treatment methods can be designed to remove phosphorus compounds which would have the greatest impact on lake biota. Physical, biological, and chemical processes responsible for returning potentially available hypolimnetic and sediment phosphorus to euphotic zones should be quantified and compared to that from external phosphorus sources. This information is required to determine relative effects of reducing phosphorus inputs to the lake system.

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CHAPTER III

BACTERIAL DYNAMICS AND PHOSPHORUS CYCLING

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The cycling of nutrients through the bacterial component of aquatic food webs is poorly understood. This lack of understanding can be attributed, in part, to the wide variety of metabolic activities associated with bacteria. These processes include: decomposition, mineralization, remineralization, heterotrophic uptake, nutrient release, and nutrient uptake (Paerl 1978, Faust and Correll 1976, McFeters et al. 1978, Ramsay 1976). Such broad descriptors of microbial activity suffer from having vague definitions which further obscure the true role of bacteria in the aquatic environment. The purpose of this chapter is to present a review of nutrient cycling in aquatic bacteria and demonstrate where fundamental deficiencies in information lie. Particular emphasis will be placed on the cycling of phosphorus in fresh waters.

The confusion of using an imprecise term to describe a particular process can be partially avoided by using the simple conceptual model of Barsdate et al. (1974). This model, shown in Figure 1, identifies the important nutrient pathways of the phosphorus cycle in bacteria. The model need not be restricted to the cycling of phosphorus as it illustrates the pathways of most elements important in bacterial metabolism. For the purposes of this chapter, movement of elements from water to surplus pool via r1 will be called nutrient uptake; this uptake can involve either organic or inorganic compounds. Movement of elements from bacterially bound pool or surplus pool to water via r4 and r2 will be called nutrient release, which can also be organic or inorganic compounds. Grazing of bacteria includes movement from surplus pool or bound pool to protozoan pool via r7 and r9. Pathways r8 (release by grazers) and r6 and r5 (movement from water to the detritus pool) are discussed in other chapters.

NUTRIENT UPTAKE

Uptake of organic compounds (via pathway r1) by bacteria is one of the most common measurements made in aquatic microbiology. This process has led to the development of several techniques where dissolved radioisotope tracers are "fed" to bacteria and uptake rates measured. Initially begun by Parsons and Strickland (1962), and refined by Wright and Hobbie (1966), this method has been used extensively in most types of aquatic environments with a large variety of organic substrates (Allen 1969, Brown et al. 1978, Crawford et al. 1974, Hamilton and Preslan 1970, Vaccaro and Jannasch 1966, Berland et al. 1970). The net conclusion from these experiments is that bacteria are capable of utilizing a variety of organic substrates at relatively low concentrations (10^{-8} to 10^{-10} M). Although uptake has been measured in many aquatic environments, a consistent pattern has not been found. The variability in reported uptake rates of different organic compounds indicates that any one estimate of uptake rate may not be representative of a large number of aquatic environments; the heterogeneous distribution of aquatic bacteria requires more reliance on empirical results rather than on estimated rates (Jones 1977).

The limited usefulness of the measurement of bacterial uptake of organic compounds stems, in part, from problems with techniques. The Wright and Hobbie (1966) method requires the assumptions that uptake of a high concentration (relative to natural concentrations) of organic substrate is uniform over several hours (duration of the experiment) and that it follows simple enzyme kinetics. Contemporary thinking (Williams 1973, Azam and Holm-Hansen 1973) discounts the possibility these assumptions can be met in a heterogenous

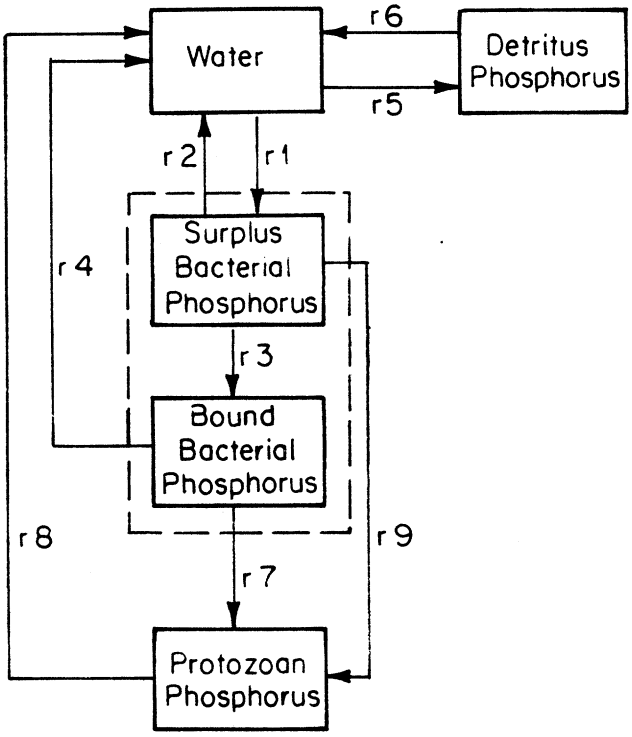

Figure 1. Conceptual model of the phosphorus cycle through bacteria. The transfer rates among the important phosphorus pools are indicated as r1 through r9 in the figure (from Barsdate et al. 1974.)

natural bacterial community. Wright and Hobbie's technique was modified to include a respiration correction (Hobbie and Crawford 1969). Most recent methods favor short incubation periods with substrate concentrations very close to natural levels (Williams 1973, Azam and Holm-Hansen 1973) and also include a respiration correction (Dietz and Albright 1978).

The distinction between the new method (Dietz and Albright 1978) and the Wright and Hobbie (1966) method is that in the new method true flux is estimated while the Wright and Hobbie (1966) technique only measures gross uptake of the substrate at best. The gross uptake is usually reported in terms of turnover times which have little ecological meaning. Turnover times are only valid when the rate of substrate uptake does not change throughout the entire turnover time period. Because many turnover times are several days in length, it is unlikely that uptake rates remain constant for the turnover time period (Williams 1973). The new method uses natural levels of substrates and gives results much closer to true ecological fluxes and also produces more reproducible results (Azam and Holm-Hansen 1973).

Irrespective of which technique is used, the evolution of the measurement of nutrient uptake by bacteria will continue. This evolution of the measurement of organic uptake by bacteria has slowed progress in understanding the true metabolic activity of aquatic bacteria. Each different technique provides a different estimate of bacterial nutrient uptake which is not necessarily comparable to previous estimates. For now, the only conclusion concerning uptake is that aerobic bacteria do take up a variety of organic substances at low concentrations in either the dark or light.

The uptake of inorganic compounds by bacteria also has been measured (Paerl and Lean 1976, Rhee 1972, Phillips 1964). The experimental errors involved in the measurement of inorganic uptake exceed those with organic uptake. For instance, inorganic P uptake is often measured as "soluble phosphate" which is an imprecise chemical descriptor. A major difficulty in measuring inorganic phosphorus uptake is the rapid rate of uptake and turnover and competition between bacteria and algae for the same resource; thus experiments where ^{32}P or ^{33}P are added to natural populations may be difficult to interpret because of interspecific uptake. Paerl and Lean (1976) and Rhee (1972) demonstrated relatively rapid movement of inorganic P into bacteria followed by slower movement into algae. Similar to the uptake of organic compounds, bacteria are capable of taking up inorganic P compounds at very low concentrations (Rhee 1972).

Bacteria unquestionably utilize organic substrates for metabolism (ZoBell 1946). These high-energy compounds are the primary source of energy for heterotrophic organisms. On the other hand, the uptake of inorganic compounds by bacteria is not fully understood. Presumably bacteria would only take up inorganics to balance their C-N-P ratios. Yet the uptake of inorganics by those organisms which are supposedly "decomposers" seems inconsistent. Would bacteria attempt to take up the same compounds they are releasing back to the water? This paradox, analogous to the extracellular release mechanism in phytoplankton, will require careful analysis before satisfactory conclusions can be reached.

NUTRIENT RELEASE

The release of nutrients by bacteria (via pathways r2 and r4) in either organic or inorganic form is the essence of microbial decomposition. Yet this very important process has been difficult to quantify. Bacterial activity is influenced by temperature, availability of substrate, and chemical composition of the substrate (DePinto and Verhoff 1977, Foree and Barrow 1970). Jones (1972a) demonstrated the relationship between senescent algae and bacterial biomass; a rapid increase in the amount of decaying algal cells in the water column, such as when a phytoplankton bloom declines, is usually followed by an increase in bacterial biomass.

Despite large variability in decomposition rates, some preliminary estimates of inorganic release by bacterial metabolism have been made. Field estimates of P turnover have been particularly inaccurate in that liberated P is rapidly re-used and rarely measured as available soluble P. Fuhs (1973) and Charlton (1975) estimated that water column P was recycled from 10 to 34 times during one growing season. Fallon and Brock (1979, 1980) have estimated that 60-70% of the organic matter from decaying phytoplankton was decomposed in the water column, primarily in the epilimnion. These studies indicated that very little phosphorus was returned to the water column from anaerobic benthic release, as these lakes were highly stratified and had little vertical mixing. Evidently, this active recycling of P in the water column was a consequence of zooplankton excretion and active release from bacterial decomposition of detritus.

More exact rates of P release by bacteria are available from laboratory studies. Golterman (1973) found that 70-80% of the organic P released by algal autolysis was converted to inorganic forms within a few days. Depinto and Verhoff (1977) conducted a study of the regeneration of P and N in axenic algal cultures and bacteria-algae cultures. They found the P released as inorganic soluble reactive phosphorus was very slow when the axenic cultures were placed in the dark. On the other hand, the bacteria-algae mixtures liberated up to 75% of the total P pool after several weeks. The rate of regeneration of the soluble P was a function of the initial P composition of the algae; P-limited algae produced regeneration rates of 0.06-0.08 µg P/mg algae (dry weight)/day, while algae growing in P-rich media produced regeneration rates of 0.16-0.39 µg P/mg algae (dry weight)/day. DePinto and Verhoff (1977) stated that excess cellular P is stored in algae in an inorganic state. This would explain the much higher P regeneration rates from algae in a P-rich environment. Therefore, bacterial crops associated with large P-rich algae communities would likely be adapted to high levels of inorganic P while bacteria associated with P-limited algae would have slower regeneration rates and use more organic compounds for their P source.

The release of nutrients under anaerobic and aerobic conditions is entirely different. In the absence of oxygen, only reduced compounds such as methane or hydrogen sulfide can be released (Lerman 1978). Anaerobic metabolism is extremely important in the sediments and at the sediment-water interface of some lakes (Wetzel 1975). But, for most lakes and the oceans the entire water column is oxygenated, confining anaerobic nutrient release to a small portion of the water body.

Although the rate of nutrient regeneration by bacteria is relatively poorly quantified, some effort has gone into incorporating this term (or function) into aquatic ecosystem models. Initially, the simple first-order

rate coefficient of "phytoplankton decay," usually as a function of temperature, was used in the models (Thomann et al. 1975). Additional models required the refinement of this term (as with Lehman et al. 1975), until bacterial activity has been treated as a complete sub-model (Clesceri et al. 1977, Bloomfield 1975). The modeling of P cycling in aquatic ecosystems is discussed in more detail in Chapter VIII. The state-of-the-art in aquatic models indicates that bacterial regeneration of inorganic nutrients is apparently a combination of substrate form and availability, water temperature, bacterial biomass, and bacterial composition (DePinto 1979). Extensive laboratory and field analysis will be needed before more precise models can be developed.

NUTRIENT REDISTRIBUTION

The advent of the epifluorescent method for counting bacteria which are either attached or free-living (bacterioplankton) dramatically changed the concept of where most bacteria occur. Early dogma suggested bacteria were primarily, if not exclusively, "decomposers" attached to detritus. But, the epifluorescent techniques developed by Bell and Dutka (1972), Zimmerman and Meyer-Reil (1974), and Hobbie et al. (1977) indicated that the vast majority of bacteria are bacterioplankton (Palumbo and Ferguson 1978). No doubt numerous bacteria are found on almost every piece of aquatic detritus including decaying algae (Paerl 1978) and fecal pellets (Ferrante and Ptak 1978). These attached bacteria could be considered the classic "decomposers," while bacterioplankton behave more like phytoplankton.

Indirect evidence suggests that bacterioplankton can alter nutrient distributions (Lean 1973, Jones 1976). Although bacteria take up primarily organic compounds while phytoplankton take up inorganic forms (Lean 1973), bacteria have been observed to readily take up inorganic P at rapid rates (Paerl and Lean 1976). Thus, bacterioplankton can effectively compete with phytoplankton for available soluble P. One major difference is that the recycle times for bacteria are on the order of minutes, while phytoplankton are capable of luxury consumption and internal storage (Rhee 1972).

The trophic dynamics of bacterioplankton and phytoplankton are slowly beginning to emerge. Jones (1971, 1972a, 1972b, 1973, 1976, 1977) has examined the interrelationships between bacterioplankton and phytoplankton in freshwaters. He finds bacterioplankton the ultimate opportunists while phytoplankton are more strategists. Phytoplankton time their growth to the ideal combination of nutrients, light, and physical conditions (Hitchcock and Smayda 1977); once ideal conditions are met, phytoplankton grow until one factor becomes limiting. Bacterioplankton often use a declining phytoplankton bloom to initiate their growth (Jones 1977). The increased substrate, both POM (particulate organic matter) and DOM (dissolved organic matter), presumably serves to stimulate the bacterial bloom.

These growth strategies have large implications for nutrient cycling in aquatic environments. Bacterioplankton readily convert large amounts of DOM, originating from either algal lysis or extracellular release, into POM (as bacteria). DePinto (1979) discussed how these nutrients, taken up by the bacteria, in turn may be released to the water column as readily available inorganic nutrients. Thus, as an algal bloom dies off, the bacterioplankton consume a large amount of the available nutrients and maintain them in the

upper water column. Those bacteria which attack decaying algae can have an impact on the composition of the detritus settling out of the water column. For example, if bacteria do not take up every element (e.g. silicon), some will be recycled at very slow rates, while others (e.g. P, N, or C) will be regenerated much faster.

GRAZING OF BACTERIA

An important pathway (r7 and r9) for the movement of nutrients through the aquatic environment is grazing of bacteria (Barsdate et al. 1974). Bacterioplankton are rapidly grazed by small ciliated protozoans, which in turn are readily consumed by small zooplankton (e.g. rotifers). The ecological implications of the grazing of bacterioplankton have led Azam (personal communication) to postulate an entire heterotrophic food web. In this scenario bacterioplankton readily survive on DOM from the extracellular release and lysis of dying algae (observed by Jones 1977, Paerl 1978, and others). The bacterioplankton are grazed by small ciliated protozoans (Barsdate et al. 1974). These protozoans serve as ideal food sources for rotifers (J. Bowers, personal communication), which in turn are food sources for carnivores. The recycling of nutrients in this heterotrophic food web is carried out by both attached bacteria and bacterioplankton.

Barsdate et al. (1974) conducted an investigation of phosphorus cycling between bacteria and the protozoans. Using freshwater bacteria, they found relatively little inorganic P release, but substantial organic P release. The amount of P regenerated from the bacteria to the water was very sensitive to the presence of ciliate bacterial grazers. When bacteria were present in microcosms alone or with small amounts of algae, regeneration rates of inorganic P were similar to those of P-limited algae-bacteria cultures measured by DePinto and Verhoff (1977). But, when protozans were added as grazers in the Barsdate et al. (1974) microcosms, the inorganic P regeneration rates were too low to measure. Thus, according to Barsdate et al. (1974) and Fenchel and Harrison (1976), the concept of bacteria releasing large amounts of inorganic P as "decomposers" may be incorrect. However, these studies cannot be considered exhaustive, particularly in that the experiments were conducted in microcosms and included only one species of protozoan.

The grazing of bacteria attached to detritus has also been suggested as an important nutrient pathway (Paerl 1978). Detritivores have been observed to consume large amounts of detritus coated with bacteria (Paerl et al. 1975). Some researchers postulate that detritivores harvest detritus as a convenient method of consuming bacteria rather than obtaining nutrients from the detritus itself. The dynamics of grazing of bacteria are not well understood (see Chapter IV for more information on herbivorous grazing). While most of the bacterial grazers have been identified, the type of bacteria commonly grazed, the percent of the population grazed, and the temporal pattern of the grazers are unknown.

BENTHIC BACTERIAL PROCESSES

The activity of benthic bacteria is probably the least understood of all bacterial processes. The benthic substrate of aquatic environments provides a diverse habitat in that anaerobic sediments are in contact with aerobic sediments and/or the overlying waters. As mentioned earlier, anaerobic and aerobic bacteria are very different with regard to the compounds they take up and release. As a consequence of this difference, "decomposition" by the benthos can provide a broad variety of nutrients to the overlying water. Benthic bacteria microbial activity has been identified with P release (Ayyakkannu and Chandramohan 1971). Presumably, benthic bacteria are responsible for the cycling of all elements which reach the sediments. This assumption can be made from mass balance calculations, as well as some direct measurments of near-bottom nutrient fluxes. Fallon and Brock (1980) show that in Lake Mendota decomposition of blue-green algae occurs in both the water column and the surface of the sediments; 57% of the decomposition occurs in the water column, and 32% at the sediment surface. However, a wide variety of benthic organisms are known to actively "work" the substrate (see Chapter VI). These organisms must be responsible for some of the near-bottom nutrient flux. The true activity of benthic bacteria remains in doubt. Jannasch and Wirsen (1973) claimed that the low temperatures and/or high pressures of the deep sea inhibit bacterial activity and cause aphotic decomposition or remineralization to be a slow process. Azam and Holm-Hansen (1974) refuted that claim with data showing considerable heterotrophic activity in the deep sea.

The actual site of the majority of nutrient regeneration is unresolved. Benthic bacteria cannot account for all of the recycling. The benthic microbial biomass is too low in comparison to bacterioplankton biomass on a M^2 basis (Holm-Hansen 1969). The primary site of the recycling of some nutrients (such as P) is most likely the water column, while for other elements it is the sediments (Kobori and Taga 1979). Fallon and Brock (1980) indicate that very little (<10%) of the organic matter from phytoplankton remains in the sediment. Most of the decomposition occurs in the water column, and the material that does reach the sediment primarily decomposes at the sediment-water interface.

SUMMARY

Progress in understanding the cycling of nutrients through bacteria has been slowed, in part, by a lack of adequate experimental techniques. Some of these technical problems stem from the difficulties of separating bacteria from phytoplankton either with biochemical or mechanical techniques. As long as this imprecise separation continues, true nutrient uptake and nutrient release rates will evade researchers. The most recent gains in the state-of-the-art in ecological aquatic bacteriology have been in enumeration. A considerable number of new, innovative techniques will be required before satisfactory progress is made in understanding nutrient cycling through aquatic bacteria.

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CHAPTER IV: LOWER FOOD WEB DYNAMICS

CYCLING OF P AMONG PHYTOPLANKTON, HERBIVOROUS ZOOPLANKTON, AND THE LAKE WATER

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INTRODUCTION

Dissolved phosphorus in lake water includes the immediate source of an element vital to primary biological production. For that reason substantial efforts have been undertaken to quantify rates of flux between dissolved pools and the biota. Particular interest has been focused on reactions involving the phytoplankton, which are the base of the trophic pyramid in pelagic communities. A guiding premise of the work reported here is that the interactions and the kinetics of processes in these systems can be understood only by perturbing the system in some way and measuring the results. This may be through massive additions of P to a lake (Einsele 1941; Nelson and Edmondson 1955; Schindler 1975, 19977) or through the use of bioassays or tracer techniques. The latter methodology was pioneered at the whole lake level by Hutchinson and Bowen (1950), Hayes et al. (1952), and Rigler (1956), from whose work and through subsequent re-interpretations (Rigler 1973) it became very clear that exchanges between dissolved and particulate phases occurred on the scale of minutes. Interest in the rapid removal of tracer-PO_4 from solution spawned the Rigler bioassay (Rigler 1964, 1966, 1968) in an effort to quantify true concentrations of dissolved orthophosphate in lake water, and led ultimately to the model by Lean (1973) of P-exchange among several functional pools.

RAPID EXCHANGE FLUXES

Basing their rationales on the demonstration that the most biologically active pools of dissolved P in lake water are often much lower in concentration than traditional chemical analyses indicate, one school of research has focused on the kinetic events that follow the addition of carrier-free radiophosphorus to lake water or algal cultures (Lean 1976, Lean and Nalewajko 1976, Nalewajko and Lean 1978). By charting the quantity of radiophosphorus that remains in solution over a time course that may span only minutes, it is possible to compute rates of exchange between P in the water and in the algae. Because the results show that the dissolved tracer P turns over so rapidly in natural waters primarily as a result of biological mechanisms, there is a tendency to regard this behavior as the fundamental process controlling the concentration of phosphate. Whereas this may indeed prove to be the case, it provides no insight to the flux rates responsible for biological production in lakes. What is measured in these experiments is isotope equilibrium only, not mass flux associated with de novo synthesis of biomass. The technique measures only one side of a two-way flux, and thus the results cannot be included in the same category with net fluxes resulting from excretion or autolysis of cells.

In fact, the guiding assumption in the studies is one of virtual steady state for mass influx and efflux, an equilibrium system into which temporary isotopic disequilibrium is introduced. The measurements essentially quantify the unidirectional movement of molecules across a cell membrane, even though an equal number of molecules are moving simultaneously in the opposite direction, resulting in zero net flux. The isotope technique consequently helps identify a freely exchangeable pool of P that is associated with living cells, and the kinetics permit the size of the pool to be estimated. To identify processes and rates that are responsible for accrual of phytoplankton biomass, net rates of flux between the water and the cells must be measured. Organisms that

divide once per day must have the means to double their cellular P contents each day also. The issue moves, therefore, to time scales and to nutrient concentrations for which it is possible to measure rates of influx that substantially exceed efflux from the cells.

RESPONSES TO ADDED SUBSTRATE

The mechanisms of transport-mediated nutrient uptake and uptake-controlled cell growth have been reviewed recently by Button (1978). Uptake of P and incorporation in cellular biomass must be viewed as a several stage process involving external concentrations of P (P_{out}), a transport component (T), a labile internal pool of P (P_{pool}), and structural cellular constituents (P_{cell}). Reversible formation of a substrate-transport complex is the intermediate step between equilibration of the internal and external substrate pools:

$$P_{out} + T \leftrightarrow TP_{out} \leftrightarrow TP_{pool} \leftrightarrow T + P_{pool} \qquad (1)$$

The internal pool comes into dynamic equilibrium with both P_{out} and P_{cell}, and sets the rate of cellular synthesis:

$$P_{pool} \leftrightarrow P_{cell} \qquad (2)$$

P_{pool} and P_{cell} each consist of components that vary somewhat independently of each other (Rhee 1973, 1974), but this generalized scheme is an adequate description of events. This scheme makes clear the point that rates of uptake of P from solution do not directly control growth rate. When cells are at steady state with constant ambient concentrations in a chemostat, rates of uptake can indeed be calculated from growth rates and cell quotas of P (e.g., Rhee 1973, 1974), but when external concentrations are changing, that approach is unsatisfactory (e.g., Burmaster 1978). The cell quota (the amount of nutrient per cell) changes in response to environmental conditions, and it is closely linked to growth rates (Droop 1968, 1973, 1974; Fuhs et al. 1972; Brown and Harris 1978). The allocation of cellular P among different molecular fractions including polyphosphates and nucleotide-P has been examined occasionally (e.g., Rhee 1973, 1974) as has the presence of extractable surplus P (Fitzgerald and Nelson 1966). The precise nature of the exchangeable pool, here called P_{pool}, is not known precisely, but it constitutes only a small part of total cellular P (Rigler 1973), and is apparently not the place where surplus P is stored. Much of the surplus P may be stored as polyphosphates, some in polyphosphate bodies in cell vacuoles or elsewhere (Harold 1966, Jensen and Sicko 1974, Stewart 1977, Sicko-Goad and Stoermer 1979).

Droop (1973) avoided the issue of identifying separate cellular nutrient compartments when he advanced the cell quota as though it were the determinant of nutrient-limited algal growth and illustrated the empirical validity of the relationship

$$\mu = \mu_m (1 - k_Q/Q) \qquad (3)$$

for P-limited growth of algae. μ is cellular growth rate (d^{-1}), μ_m is the theoretical maximum rate, Q is the cell quota (μmol P $cell^{-1}$), and k_Q is the minimal amount of P necessary for cell division. Other authors have discounted

the general validity of this approach by demonstrating that for other nutrients, particularly C, N, and sometimes Si, Eq 3 is a poor description (Caperon and Meyer 1972, Goldman et al. 1974, Goldman and McCarthy 1978) unless μ_m is regarded as a purely fictional parameter not even remotely similar to the maximum growth rate that can be estimated for cells in steady state growth. There is no a priori reason to suspect that P should obey one growth model and that other potentially limiting nutrients should obey another; the discrepancies arise because cell quotas are not only determinants of growth rates, they are products of them, too, and because some nutrients are subject to much greater variability in the cell than are others (Goldman and McCarthy 1978).

Button (1978) solved the relevant equations to evaluate the kinetics implicit in Eq 1 for the general case. What emerges is a scheme in which active transport, molecular diffusion, and product inhibition are all involved to some extent. Growth rates are controlled by rates of supply of nutrients from the water only to the point at which intracellular conversion of available nutrient into structural components becomes the rate-limiting step. Maximal rates at which P can be transported into the cell may be many times greater than P can be utilized once it gets in the cell. This means that concentrations at which growth rates become saturated will be much lower than concentrations required to saturate the uptake mechanisms (Lehman et al. 1975, Button 1978, Burmaster 1979).

Net rates of nutrient uptake are usually evaluated by Michaelis-Menten kinetics:

$$u = u_m \cdot P_{out}/(K_P + P_{out}) \qquad (4)$$

where u is uptake rate (maximum $u = u_m$), and K_P is the half saturation constant for uptake. The model in Eq 1 implies that flux rates may deviate from these simple kinetics under some circumstances (Button 1978). Brown et al. (1978), in fact, demonstrated empirically that rates of uptake proceed faster at low concentrations of PO_4 than would be expected by fitting a Michaelis-Menten curve to data obtained at higher concentrations and extrapolating down to the low values. The effect does not seem caused by the rapid exchange fluxes discussed earlier, and may imply the existence of several transport systems in algal cells, each with a differing affinity for dissolved PO_4. The rapid exchange between P_{out} and P_{pool} does suggest that there could be a concentration of P_{out} for which net uptake is zero, but the affinities of the transport system are so great that the relevant concentration, if it exists, would defy conventional methods of chemical analysis.

Another source of deviations from simple uptake kinetics is the diffusion limitation that could occur at low phosphate concentrations (Munk and Riley 1952, Pasciak and Gavis 1974, Gavis 1976). Molecular diffusion in the boundary region around a cell might not be rapid enough to maintain high flux rates at the cell surface regardless of the affinity of the transport system. These effects can be very important when ambient concentrations are low, in which case sizable concentration gradients needed to maintain rapid diffusive flux cannot be established. Because some methods indicate that ambient concentrations of PO_4 may be very low (see Rigler 1973), this issue may be important in lakes.

Although there are reasons to suspect that simple Michaelis-Menten kinetics do not give an adequate description of uptake rates at low

concentrations, the half saturation constant K_p obtained from that kinetic analysis is still regarded as a good measure of the affinity of the transport system. Ranges of K_p have been documented for many species (see summaries in Healey 1973, Lehman et al. 1975), and they raise some important questions. For instance, in all cases the half saturation constant is much greater than the concentration usually encountered on average in solution. Does this mean that the uptake system is always far undersaturated? If so, what is the adaptive advantage of possessing a system with so much unused capacity? A key consideration is that the maximum possible rate of uptake of P is usually far greater than necessary to support the maximum possible rate of cell division. It follows that luxury uptake of P (uptake and storage of P beyond immediate cellular needs) could be a common occurrence. In fact, if saturating concentrations are encountered rarely but dependably, luxury uptake may be a prime mode of sustenance, as will be discussed later.

NUTRIENT RELEASE TO THE DISSOLVED PHASE

When the nutritional demands of phytoplankton are estimated from primary production data or from nutrient uptake it has been observed that the cells are utilizing inorganic nutrients at rates far greater than the substances are being supplied from external sources or from ambient dissolved pools (Barlow and Bishop 1965; Ganf and Blažka 1974; Lehman 1978, in press; Richey 1979). Some of the demand for nutrients must be sated by nutrients cycled within the water column. Two alternative mechanisms have been proposed to account for the requisite fluxes. Some authors claim that physiological death of phytoplankton is such an important event (Jassby and Goldman 1974) that autolysis, possibly aided by microbial attack on moribund cells, can account for most of the recycling (Golterman 1973). Whatever its cause, cell death and lysis release phosphate rapidly to the water, probably because of the labile nature of phospho-ester bonds, and the autolytic enzymes present in the cells. The rapid efflux of P from living cells detected during isotope equilibrium experiments (e.g., Lean and Nalewajko 1976) probably represents diffusion of molecules from high concentrations inside the cell membrane.

An alternative source for the nutrients is regeneration from the algae indirectly, through the grazing activities of herbivorous zooplankton. Nutrients are regenerated to dissolved pools either by excretion or by the breakdown of incompletely digested remains of egested algal cells. The liberated nutrients are very reactive biologically, and they are available not only to the preferred prey of the herbivores, but also to their competitors. To illustrate the impact that nutrient release from zooplankton can have on the phosphorus cycle in lake water, it is useful to review what is known about the mechanisms and rates of feeding and metabolism.

FEEDING BY ZOOPLANKTON

Empirical investigations have demonstrated that grazing can influence the composition and abundance of algal communities (Cushing 1963, Haney 1973), particularly during the late spring and summer. Also well documented is the fact that the grazers are very selective about the types of particles they ingest (Arnold 1971, Nival and Nival 1973, Berman and Richman 1974, Richman

et al. 1977). Some of the selection may be dictated purely by the mechanical properties of the filtering apparatus (Nival and Nival 1976, Boyd 1976), but there may also be a high degree of chemosensation and decision-making involved (Poulet and Marsot 1978). The favorite procedures for measuring feeding rates rely either on direct quantification of changes in abundance of the food particles (e.g., Reeve 1963, Frost 1972), or on incorporation by the animals of a radioactively labelled food (e.g., Rigler 1961b, Geller 1975). Early workers believed that filter-feeding zooplankton were completely automatic, in the sense that each animal would always filter a constant volume of water, regardless of the concentration or types of particles it contained (Fleming 1939, Harvey 1942). Studies by Ryther (1954) and Marshall and Orr (1955), however, soon made it clear that at high concentrations of food particles the rate of ingestion levels off to some maximum value. Subsequent work showed that the observation held for both field and laboratory populations (Rigler 1961b, Reeve 1963, Burns 1966, Parsons et al. 1967). Several different formulations were advanced to describe the empirical results mathematically, but the choice of which equation an author used to represent his data appears to have been subjective. In the hope of finding a single "best" equation, Mullin et al. (1975a) used Frost's (1972) extensive data on feeding rates of Calanus pacificus to try to distinguish the best empirical model by statistical means. They found that the data fit the three different models they examined almost equally well.

Some authors have taken a less empirical approach to the issue, and have tried to justify grazing models from basic assumptions about feeding behavior. Cushing (1959, 1968) and Crowley (1973) derived formulations for grazing zooplankton from the same constructs that Holling (1959) used to erect a scheme for predation rates among animals in general. An alternative approach advanced by Lam and Frost (1976) and by Lehman (1976) treated grazing as an optimization process for the grazer in which effort is expended to gather food, and nutritional reward results from its digestion. Frost (1975) showed that the feeding behavior of Calanus is consistent with the optimization hypotheses, but not with the other models commonly in use. This experimental observation still awaits confirmation from other species.

Beyond the matter of feeding rates on a single food type and their mathematical representation is the issue of selectivity exhibited by zooplankton when they are presented with the array of possible food species in nature. Many authors (e.g., O'Neill 1969, Bloomfield et al. 1973, Park et al. 1974, Vanderploeg and Scavia 1979a, 1979b) have proposed that simple coefficients applied to each food source can represent both the mechanical biases of the food-gathering mechanism (passive selection, in the sense of Frost 1977), and the more active selection/rejection process based perhaps on taste (Poulet and Marsot 1978). The approach is basically sound, but the models used to represent the behavior are probably invalid for a variety of reasons. First, the animals can change their selectivity in response to the nutritional quality and abundance of available prey. Wilson (1973) and Richman et al. (1977), for instance, showed that some copepods change their selectivity in response to changes in the available particle spectrum. Second, maximal feeding rates are dependent on the food species. To some extent this is because the volume ingested plays a role in regulating feeding rates (McMahon and Rigler 1965, Geller 1975), and because different food species have distinctly different carbon-to-volume ratios. Also, there are considerable differences between species in the degree to which they are compressed inside

the gut (Geller 1975).

Once food is ingested by a zooplankter, only a fraction of it is assimilated and the rest is egested. Rates of assimilation and egestion will influence not just secondary production in a lake, but rates of nutrient cycling as well. Strong experimental evidence exists for the claim that digestion efficiencies are specific to individual food types (Lefèvre 1942, Marshall and Orr 1955, Arnold 1971, Porter 1973). Rates and efficiencies of assimilation may sometimes be identical for taxonomically dissimilar organisms like Scenedesmus, a green alga, and Asterionella, a diatom, but very different for more similar organisms like the green algae Scenedesmus, Stichococcus, and Staurastrum (Geller 1975, Lampert 1977b). Some authors have occasionally reported instances of "superfluous feeding" (Beklemishev 1962) at high food abundances. That is, much more material is ingested than the animal can possibly assimilate. Conover (1966a) and Lampert (1977b) disclaimed the occurrence of superfluous feeding among herbivorous zooplankton, but one should not conclude that assimilation efficiency is totally independent of food concentration. Schindler (1968) demonstrated that the ratio of assimilated energy to ingested energy decreases by approximately a factor of 2 when Daphnia magna is fed on progressively more concentrated diets. In other words, when food is very abundant and processing rates are rapid, digestion is less complete than when food is rare. This corresponds to Geller's (1975) observations about variable gut passage times. At low food abundances, ingested material may be retained inside the gut for more than an hour, but when external concentrations are high, food is egested within 10 minutes.

Experiments suggest that large differences in assimilation efficiency as a function of food concentrations are unlikely. Differences of a factor of 2 (Schindler 1968) or less (Lampert 1977b) are probably the full range that occur in natural populations. The picture is a little different when considering the fate of materials that are ingested but not assimilated by the animals, for a very simple reason. The fact that Schindler (1968) reported assimilation efficiencies between 90% and a little more than 40% means that between 10% and 60% of the ingested material may be returned to the water unassimilated. Regarded in this way the variability of the egested portion is much larger than that of the assimilated portion on a relative basis. The nutrients associated with this egested material are either released to inorganic pools immediately or are subsequently remineralized by microbial decomposers. Releases of nutrients caused by inefficient feeding are not confined to egestion. Lampert (1978) showed that uningested cells which are broken or damaged during filtering activities of the animal may leach dissolved organic carbon to the water. It can be assumed that nutrients such as P and N are released as well. Other investigators have reached the same conclusion (e.g., Cushing 1955, Conover 1966b, Martin 1970, O'Conners et al. 1976, Bowers and Grossnickle 1978). This mechanism may be even more important among carnivorous cyclopoid (Brandl and Fernando 1975a, 1975b) and calanoid copepods (Anderson 1970, Bowers and Warren 1978, Kerfoot 1978, Landry 1978), which leave partially eaten prey and fragments after an attack. The various fluxes associated with imperfect feeding efficiencies can be important to nutrient recycling at some times of the year. Their magnitudes must be added to those of the nutrients that are excreted to the water during the metabolism of assimilated compounds. Another consideration is that inorganic nutrient stores in the algae (e.g., luxury consumed stores of P) are probably not assimilated by the zooplankton, and these constituents are selectively egested. This means that the nutrient

ratios in the egested material may be substantially different from the ratios that are ingested.

Selective egestion is important, because there has been a long tradition of estimating rates of metabolic excretion of P from zooplankton on the basis of measured respiration rates (e.g., Satomi and Pomeroy 1968, Ganf and Blažka 1974, Devol 1979). The published O:P ratios are subject to considerable variability, which may be caused by variability in the nutritional condition of the animals (Ikeda 1977). The requisite information may be more difficult to interpret than was originally anticipated. Lampert (1975) showed that much of the carbon assimilated by Daphnia pulex is metabolized almost immediately. He (Lampert 1977a) suggested that a sizable portion of the metabolic demands of herbivorous zooplankton is met by the immediate use of newly digested food, rather than by catabolism of body constituents. This means that the P content of excreted material may not bear any simple relation to the elemental composition of the animal tissue. Peters and Rigler (1973) and Peters (1975) in fact used a radiotracer technique to infer that this was indeed the case for herbivorous zooplankton.

A better method for determining nutrient release from the zooplankton has been to measure the nutrients directly. There are problems with interpreting the results, nonetheless. Measured concentrations represent a balance between rates of nutrient remineralization by the zooplankton and the simultaneous uptake of the nutrients by phytoplankton. First filtering the algae from the water is not satisfactory, because animals without food behave differently from well-fed ones (Conover and Corner 1968, Takahashi and Ikeda 1975, Mayzaud 1976, Ikeda 1977, Lampert 1978). Similarly, concentrating the zooplankton to obtain unambiguous measurements of nutrient excretion can mean that food supplies may be rapidly exhausted, the animals may be damaged, or their physiology, including the rates and forms of excreted substances, may change (Mullin et al. 1975b). These points are of interest also in estimating the fractions of total P that are released to the water in organic and inorganic form because concentrated plankton collected with nets in the field may release as much as half of the P in organic form (Pomeroy et al. 1963, Satomi and Pomeroy 1968, Le Borgne 1973), whereas careful laboratory studies with undamaged animals find that most of the release in short-term assays is PO_4 (Rigler 1961a, Butler et al. 1969, Peters and Lean 1973, Ferrante 1976).

TIGHT BIOTIC COUPLING OF RELEASED NUTRIENTS

Despite potentially rapid rates of nutrient remineralization from a variety of causes, the concentrations of dissolved P in lake waters usually remain very low during the seasons of highest productivity. One reason that released nutrients do not accumulate in the water is they are swiftly removed by the algae and used to enhance their growth. Cycling fluxes intensify and less algal biomass is needed to maintain a given level of productivity; new biomass is generated just as quickly as the old biomass is consumed or lysed and the nutrients are regenerated. Despite low average concentrations of dissolved nutrients, algae may sometimes be dividing at rates close to their physiological maximum, fueled by the rapid biotic cycling of P and N (Goldman et al. 1979), where the emphasis this time is on net fluxes, not the two-way fluxes that simple isotope equilibrium experiments show. There are two mechanisms by which this can happen. On the one hand, uptake rates at low

concentrations of P may be much greater than would be expected by extrapolating down from high concentrations, a possibility that has already been discussed. On the other hand, the scheme might be precisely the one that Goldman et al. (1979) envisage, with algae encountering very heterogeneous microenvironments only micrometers in size, some of which are severely enriched with nutrients owing to remineralization events. If nutrients are rapidly sequestered by the cells in these episodic and disjoint patches and then subsequently used for growth (luxury uptake), mean ambient concentrations would indeed remain low and yet be perfectly consonant with rapid cellular division rates. If one can safely assert that zooplankton are dominant agents of nutrient release at some times or places, then this scheme becomes plausible.

Nutrient release from the zooplankton is ultimately tied to their feeding rates. Some of the nutrients assimilated by the herbivores and used for growth and reproduction contribute to fluxes through higher trophic levels, but most of the assimilated nutrients are returned to solution one way or another during the season. Activities of the grazers cause selective mortality to the phytoplankton on the one hand, and fertilization on the other. The effects of the animals on rates of competitive displacement of algal species due to differential growth rates are potentially much greater than those caused by grazing losses alone. Nutrients released to the water as a consequence of the activities of the animals are available to all the algae, not just to the preferred prey of the grazers. This means that herbivores can depress the abundances of some algal species through selective grazing, and enhance productivity of others by nutrient release.

The best estimates for rates of feeding and of nutrient release have been obtained from relatively large crustacean zooplankton, particularly cladocera and calanoid copepods. Smaller herbivores have faster metabolic rates per unit biomass. This means that rotifers and protozoa, for instance, deserve careful attention. If the biomass of these small metazoa and protozoa is substantial in any water mass, their impact could be considerable. Gliwicz (1975, 1976) reported that rates of primary production in two tropical lakes are closely correlated to the grazing activities of herbivorous zooplankton, and Lehman (1978, in press) found that nutrient release by zooplankton can supply a major share of the nutritional requirements of epilimnetic phytoplankton in a temperate lake during the summer, an observation corroborated by Devol (1979) for the same lake by independent means. Rapid cycling of nutrients between grazers and algae promotes high rates of primary production and cell division at times when allochthonous inputs and dissolved pools could not support populations for even one full day.

SUMMARY

Processes responsible for biotic cycling of phosphorus in the water column are receiving increased attention in light of discoveries that external sources of nutrients are sometimes insufficient to explain observed rates of biological production in lakes. The chief difficulties slowing a rapid and complete analysis of the system are primarily technical ones that arise because fluxes associated with production and with losses are intimately connected.

Only the outline of a picture characterizing focal processes in phosphorus cycling is known at present with great assurance, but that outline provides a guide for future work. A detailed kinetic description of nutrient uptake by

assemblages of natural phytoplankton at concentrations slightly above ambient is a vital need. Additional research needs are measurements of nutrient release *in situ* by the zooplankton, including not just juvenile and adult crustaceans but rotifers and protozoans as well. Particularly important are effects of age-structure and species composition on the flux rates anticipated through seasons, and from year to year. The contributions of microzooplankton have been poorly studied in proportion to their likely importance. Related to this issue of nutrient remineralization, and of similar critical importance, is an evaluation of mechanisms and determinants of selective grazing by herbivorous zooplankton. That line of inquiry will probably prove central to a dynamic description of events in the open water, because grazing limits the standing crop of phytoplankton and thus their overall nutrient uptake capacity. Selective grazing also represents the first step in a sequence by which nutrients are remineralized back to a biologically-reactive dissolved form by herbivores. Above all, the work must be rigorously quantitative. The issue rests no longer on identifying these pathways, or even on asserting their general importance, but rather on determining the magnitudes of nutrient and biotic fluxes in nature and integrating them into a coherent, internally consistent, and dynamic exposition of the structure and productivity of pelagic lake ecosystems.

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CHAPTER IV - CONTINUED

PHOSPHORUS CYCLING THROUGH ZOOPLANKTON AS INFLUENCED BY THEIR DIURNAL VERTICAL MIGRATION, PREDATORY FEEDING, AND POPULATION DYNAMICS

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INTRODUCTION AND BACKGROUND

One truism in ecology that sets it apart from other disciplines is that "everything affects everything else" in the ecosystem. Such is the case for the recycling of phosphorus in lakes and oceans. Virtually all biotic and abiotic components in lakes and oceans are directly or indirectly involved with the movement of this element. Zooplankton, an integral part of the pelagic community, affect phosphorus recycling in lakes primarily as grazers upon phytoplankton and predators upon themselves as well as by regeneration of phosphorus through inefficient ingestion, egestion, and excretion. Three aspects of zooplankton ecology, diurnal vertical migration, predatory feeding, and population dynamics, influence these phosphorus regenerative processes.

DIURNAL VERTICAL MIGRATION

Animal migrations, their description, selective advantage, and evolutionary origins, have long held the interest of ecologists. These regular movements occur on seasonal, lunar, semilunar, and diurnal time scales as in this case with the zooplankton. Hutchinson (1967) defined three patterns of diurnal vertical migration. Nocturnal migration, the most common pattern, begins near sunset when zooplankters ascend from daylight depths into shallower strata, remain there through the night, and then descend to daylight depths again at dawn. Rarely observed reversed migrations are the reverse of this sequence. A twilight pattern results when, after the evening ascent, a midnight sinking occurs followed by a predawn ascent. A short time later, at dawn, the zooplankters descend again to daytime depths.

What is the relationship between vertical migration and phosphorus recycling? When assessing the importance of diurnal migration, Longhurst (1976) suggested that any mass migration involving such a significant fraction of the plankton biomass has profound influences upon community metabolism. One facet of this problem is clear; to date no completely comprehensive data set over short time scales exists linking migration, feeding, and the vertical distribution of food. Until this is accomplished the coupling of phosphorus recycling to migration will remain obscure.

Diurnal migration will partially influence the spatial and temporal dynamics of phosphorus recycling by zooplankton through the effects of temperature, vertical distribution of food items, and diel feeding rhythms. Zooplankters migrating during thermal stratification often experience a diurnal rhythm in temperature. Higher temperatures will stimulate higher rates of excretion, thus creating a diurnal cycle in excretory rates. This suggests phosphorus excretion may be quite intense at night when migrators experience temperatures 5° to 10° higher than in the daytime (Ketchum 1962). A few field studies have suggested rhythmic excretion rates (Hargrave and Geen 1968, Eppley et al. 1973, Ganf and Blažka 1974), but detailed correlations between temperature and excretion through time have yet to be performed.

Besides cyclical temperature regimes, migrant zooplankters also experience radical shifts in their nutritional environment since algal and zooplankton food items will change significantly over depth in quantity and species composition (Bowers 1979). Only recently has this role of temporal and spatial heterogeneity or patchiness been perceived as crucial to understanding zooplankton nutrition (Mullin and Brooks 1976, Dagg 1977, Mayzaud and Poulet

1978). From earlier observations, excretion and egestion are highly correlated to food levels. Thus phosphorus regeneration is at least indirectly tied to migration and vertical prey and temperature distributions. Consequently, migration may induce intense pulses of phosphorus excretion and egestion when feeding rates are at a maximum during one diurnal cycle. Because herbivory (Frost 1977) and predation (Kerfoot 1977a) may be selective, feeding habits could be strongly influenced by migration and consequently linked to assimilation and egestion. How this affects phosphorus regeneration is presently not understood.

With higher temperature and food densities in surface waters, zooplankton feeding is now thought to be partially a discrete event when feeding is nocturnal (Gauld 1953, Nauwerck 1959, Mackas and Bohrer 1976, Bowers and Grossnickle 1978) or bimodal at dusk and dawn (Haney 1973, Haney and Hall 1975). Perhaps these feeding cycles are endogenously controlled (Chisholm et al. 1975, Duval and Geen 1975) and coupled to field observations of diel periodicites in excretion. Laboratory feeding experiments might clarify this relationship.

Although migrations have been thoroughly described in marine and freshwater environments (Ringelberg 1964, Hutchinson 1967, Longhurst 1976), their origin and the selective advantages that fostered them still remain unsolved. Different hypotheses have been proposed involving light (Russell 1927, Harris 1953, Hairston 1976), population regulation (Wynne-Edwards 1962), and genetic recombination (Davis 1961). More recent ideas have been based on the trophic relationships between the migrant zooplankter and its prey and predators. Since optimal times of food and temperature rarely coincide in time and space, McLaren (1963) based his hypothesis on the fact that higher egg production at colder depth strata was offset by delayed development. By feeding only at night in the warm surface waters, copepods could maximize their feeding efficiencies at higher temperatures and their growth and development at lower temperatures resulting in an energy (McLaren 1963) or fecundal (McLaren 1974) bonus for the animal. Enright (1977) also believed motivation for migration lies in the consequences of the daily alternation of temperature experienced by migrating zooplankton in thermally stratified waters. His metabolic model predicted a greater energy gain for growth and reproduction by feeding at night in the warm surface water where algal production is highest and by reducing energy demands in the daytime at the deeper (colder) depths. Another hypothesis suggests that diurnal migration evolved from the avoidance by zooplankton of daylight where they are vulnerable to visually oriented planktivorous fish. Zooplankton ascend into the surface waters at night to feed and yet avoid predation. Zaret and Suffern (1976) provided experimental evidence supporting this hypothesis in Gatun Lake, Panama, and Fuller Pond, Connecticut. A preferred prey of the planktivore in Gatun Lake always remained at depths during its nocturnal migratory cycle where light intensities were too low for the planktivore to efficiently feed. Laboratory experiments with a daphnid prey and its planktivore from Fuller Pond showed a high correlation between predation rates and light intensity. But, prey from Gatun Lake exhibit this behavior in an isothermal habitat in direct contradiction to McLaren's (1963) and Enright's (1977) thermal hypotheses. Unfortunately, definitive and testable hypotheses resolving this unusual behavior have not been forthcoming (Miller 1979).

In summary, diurnal vertical migration places strong migrators on a diel schedule where all aspects of their daily life, especially temperature,

feeding, and prey environment, are intimately linked to the movement. The P regeneration mechanisms discussed earlier (Lehman, Chapter IV) indicate that the complex migratory relationships are certainly important in phosphorus cycling.

PREDATORY FEEDING BEHAVIOR

Most of what we know about phosphorus regeneration through zooplankton is derived from experiments with herbivorous zooplankters due to their important regulation of algal dynamics (see Lehman, Chapter IV). Far less is known about predaceous zooplankters as phosphorus recyclers.

These invertebrate predators, mostly cyclopoid and calanoid copepods, are now increasingly viewed as a major structuring force of limnetic communities (Lynch 1977; Kerfoot 1977a, 1977b). Selecting for small zooplankton prey, they tend to structure the community toward larger species. Cyclopoids are herbivorous as nauplii and copepodite instars CI through CIII, then switch to carnivory as adults (Gophen 1977). The adults prefer small prey with rotifers and copepod nauplii the preferred groups (Confer 1971, Brandl and Fernando 1975a, Karabin 1978, Gilbert and Williamson 1978), although prey shape, carapace strength, prey escape responses, and palatability also affect selectivity (Li and Li 1979). Calanoid predators also prefer small fragile prey (e.g. Kerfoot 1978), but recent evidence suggests some species prefer larger prey within defined limits (Mullin 1979, Landry 1978).

Selective feeding behavior for small prey will influence phosphorus regeneration. Inefficient consumption of larger prey or "sloppy ingestion" presumably results in the release of prey viscera into the water when prey are torn apart or only partially eaten and discarded by both cyclopoids (Brandl and Fernando 1975a, 1975b) and calanoids (Anderson 1970, Bowers and Warren 1978, Kerfoot 1978, Landry 1978). Loss of dissolved phosphorus from damaged zooplankters is considerable (Eppley *et al.* 1973, Mullin *et al.* 1975). Brandl and Fernando (1975b) noted that cyclopoid assimilation efficiencies decreased dramatically when prey had to be torn apart at the mouth. Thus significant amounts of phosphorus may be lost not only during the act of feeding, but during egestion as well. Finally, size selection for smaller prey results in intense predation pressure on juvenile crustaceans and rotifers whose phosphorus excretory rates are much higher than larger prey.

Rotifers are potentially an important group in nutrient recycling. Rotifer excretion rates of dissolved phosphorus are generally higher than crustacean species (Hargrave and Geen 1968), thus, this group is considered an important component in phosphorus cycling due to their high metabolic rates (e.g. Makarewicz and Likens 1979). Since rotifers are small and relatively slow-swimming fragile prey compared to juvenile crustaceans, they are a preferred prey of carnivorous copepods. We need more information on the food web pathways they pass through and their quantitative role in phosphorus excretion.

Predaceous zooplankters excrete phosphate per unit of body weight at higher rates than herbivores (Beers 1966, Mullin *et al.* 1975). This is surprising since prey consumed by carnivores have higher bodily N:P ratios than phytoplankton (Mullin *et al.* 1975). Perhaps they excrete more nitrogen as organics compared to herbivores or assimilate phosphorus more efficiently than nitrogen. For this reason excretion by carnivorous zooplankton warrants further study.

Phosphorus regeneration through excretion, egestion, and inefficient ingestion is probably species, age, and sex specific which involves the demography of zooplankton. Allan (1976) separated the zooplankton into two groups: rotifers and cladocerans, and the copepods. The Rotifera and Cladocera are "r-selectors" (MacArthur 1972), species with high intrinsic rates of increase and adapted to seasonal or unpredictable environments. Their life history patterns are characterized by parthenogentic reproduction and short multivoltine life cycles. They form large highly variable populations reacting, without time lags, to habitat changes. Copepods are "k-selectors," which reproduce sexually at lower rates and have longer multivoltine or univoltine life cycles. They respond with relatively longer time lags to environmental changes.

Differences in population characteristics most likely translate into significant differences in phosphorus regeneration during seasonal succession in temperate lakes and marine waters. Rotifera and Cladocera are summer and fall plankton groups, in which a few species will rapidly increase in numbers for a few weeks and then decrease dramatically, to be followed by another species group re-enacting this boom-and-bust cycle. During the rapid growth phase of these cycles, which overlap throughout the summer, turnover rates (production/biomass ratios/time) are high, accounting for the majority of the phosphorus flux in the community (e.g. Makarewicz and Likens 1979). In marked contrast, the copepods have phosphorus flux rates several times lower. The effects of these spurts of phosphorus regeneration on phytoplankton growth is poorly understood. Predatory pressure on rotifers and cladocerans may indirectly control these population and nutrient regeneration pulses by triggering the succession of numerical decreases throughout the summer (Threlkeld 1979). Copepods may play a dominant role in phosphorus regeneration during the early spring when the zooplankton assemblage is dominated by naupliar and copepodite instars which have relatively higher rates of phosphate excretion due to their small size and rapid growth.

Another difference between these groups concerns phosphorus release rates from fecal material, which further emphasizes the higher phosphorus flux through rotifers and cladocerans. While copepods produce a coherent pellet wrapped in a periotropic membrane, cladocerans and rotifers produce a pellet which breaks up immediately upon excretion into the water. Intuitively, nutrient release from the rapidly broken up fecal material of cladocerans and rotifers would appear to occur at higher rates than from copepod pellets, which gradually disintegrate from bacterial attack. The copepod pellets may serve as an effective mechanism of P removal from the photic zone. Quantitative studies comparing these differences are needed.

SUMMARY

Although no complete theory concerning the selective advantages of vertical migration is imminent, feeding strategies and predator avoidance by zooplankton will be fruitful directions for future research. Comprehensive field efforts would further our insights into this behavior, and begin to reveal the effects of the migrations on phosphorus regeneration. Excretion and egestion rates have been observed to increase with higher temperatures and food

densities when zooplankton ascend at night to feed in the warmer and more productive surface waters. These discrete periods of intense feeding could induce pulses of phosphorus release. Laboratory experiments correlating phosphorus regeneration to temperature and feeding cycles, and field efforts coupling migration to zooplankton ingestion rates and phytoplankton patchiness, should be a principle research objective.

Invertebrate predators play an important known role in structuring limnetic communities, but their effect on phosphorus recycling is virtually unknown. Two studies indicate that predatory copepods excrete phosphorus at higher rates than herbivorous species. Inefficient ingestion of rotifers and crustacean nauplii by predaceous cyclopoids is a potentially important but unexplored mechanism for phosphorus release. Laboratory experiments designed to address this behavior and predator excretion rates are needed.

Successive blooms of rotifers and cladocerans during their summer species succession could account for a significant fraction of the phosphorus regeneration in temperate lakes. Excretion and egestion rates during these blooms should be highly correlated to the reproductive dynamics of these groups. The effect of rotifers, in particular, are unclear in this succession and, due to their very high production rates, deserve special attention.

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CHAPTER V

FISH DYNAMICS AND PHOSPHORUS CYCLING IN LAKES

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INTRODUCTION

Principles of the predation process and their application to phosphorus cycling in lentic environments are summarized in other chapters of this document (e.g. Lehman Chapter IV, Nalepa et al. Chapter VI, and Scavia Chapter VIII). The special case for fishes is primarily expressed in two ways. (1) Fishes have long life histories relative to the kinetics of P cycling; their modulating effects are second only to the "big-slow" component of sediment-water exchange rates and, where appropriate, to the flushing rate of a lake (O'Neill 1976). (2) Fish populations are the object of management manipulations. For example, natural reproduction of Great Lakes salmonids and the sea lamprey are continually altered through fisheries management: salmonid stocks are regularly enhanced from hatcheries as recruitment although natural reproduction is modest or non-existent; lamprey populations are maintained at minimal levels through continuing use of lampricides. Consequently, the quantitative effects of predation by fishes are largely controlled through management practices.

Recent synthesis papers addressing the role of salmonid predation in structuring Lake Michigan's fish assemblage (Stewart et al. unpublished manuscript) and the continuing lamprey control program (Walters et al. 1980) advocate an experimental approach for management programs. If carefully conceived, modeled, and monitored, such whole system experiments could provide major insight into phosphorus dynamics.

The role of fishes in phosphorus cycling is the subject of two recent reviews (Kitchell et al. 1979, Nakashima 1980). The role of fishes may be generally described under four major headings: (a) excretory remineralization of P, (b) storage and translocation of P, (c) selective predation by fishes, and (d) predator effects on community structure. Each topic will later be discussed in greater detail. The massive dilution and mixing rates of Great Lakes waters reduce (a) and (b) to relatively minor status. Although massive mortality (e.g., alewife die-offs) may result in substantial fertilization, the effects are local and of lesser significance than continuously acting and potentially dynamic processes such as those associated with the role that fishes play as predators.

Selective predation processes substantially determine the size-particle distribution of prey trophic levels. Phosphorus flux rates are typically inversely related to mean particle size. "Keystone predator" (Paine 1966) or polyphagous predator (Hassell 1978) effects on communities become apparent as dominant competitors are selectively removed by predation, thereby allowing coexistence of a more diverse species assemblage including a variety of life history strategies.

The results of experimental studies (Hurlbert et al. 1972, Cooper 1973, Bartell 1978) have shown that consumer effects are significantly non-linear. For example, at low predator densities, predation plays a minor role in nutrient cycling or primary production processes. At intermediate predator densities, however, the predation process can dramatically stimulate nutrient cycling rates and enhance productivity per unit of nutrient. In general terms, the mechanism is manifest as a series of predator-induced mortalities and selection processes that reduce competitive interactions between the prey, thereby maintaining prey populations in the logarithmic growth phase. As a consequence, turnover rates remain rapid, a diversity of life history strategies is sustained, and P cycling efficiencies are high. But at very

intense levels of predation, prey biomass can be substantially depressed, and local extinctions will result in reduced diversity and lower ecological efficiencies. Production processes can be either highly variable or severely depressed (Kitchell et al. 1979).

PHOSPHORUS REMINERALIZATION BY FISHES

Excretion

Estimates of rates of phosphorus excretion as well as attempts to measure forms of P excreted are rare. Equally important, variability is substantial. Furthermore, excretion and egestion are often not separated, and the several techniques employed yield rather different results. Short-term measures (1-3 hr) of excretion by recently captured fish generally yield high rates but are suspect due to the unknown effects of capture stress and handling (Nakashima 1980). Whitledge and Packard (1971) reported excretion rates of phosphorus from anchovies in Pacific upwelling regions of 2.1 mg phosphorus g^{-1} day^{-1} on a dry weight basis. For a variety of marine fishes at high temperatures (>15°C), Pomeroy and Kuenzler (1969) found an excretion range of 0.008 to 0.4 mg phosphorus g^{-1} day^{-1}. Excretion rates similarly derived for carp range from 0.25 to 0.27 mg phosphorus g^{-1} day^{-1} (Lamarra 1975). Based on measures of P release during starvation (1 week) of bluegill sunfish, Koonce and Seadler (unpublished manuscript) obtained a mean excretion rate of 0.033 mg phosphorus g^{-1} day^{-1} at 17°C.

Based on laboratory studies of bluegill sunfish, excretion was found to account for 48% of the total phosphorus released by both excretion and egestion (Koonce and Seadler, unpublished manuscript). Estimated by difference, P excretion by yellow perch was 2-71% of total for excretion plus egestion: the average of 15 trials was 50% (Nakashima 1980).

In general, rates of P excretion are modest compared to excretion by zooplankton. However, a dense school of fish may create local enrichment (Whitledge and Packard 1971). The relative importance of this special case remains undetermined for freshwater systems.

Egestion

Due to their rapid sinking rates, fecal pellets represent a potentially important mechanism where material consumed in the pelagic zone is lost to the sediments. Zooplankton fecal pellets are known to be a significant vector in marine systems (Turner and Ferrante 1979) and in some lakes (Kitchell et al. 1979). As specific consumption rates of fishes are substantially less than those of smaller animals, the quantitative role of fecal pellet losses are undoubtedly less, but have been estimated by Nakashima (1980) to be 10-25% of total daily sedimentation losses in Lake Memphremagog. Herbivorous fishes in shallow water habitats increase net sedimentation of detrital phosphorus (Terrell and Terrell 1975) thereby increasing P concentration in surface sediments (Stanley 1974). The relative importance of the mechanism remains rarely estimated and will vary with the food habits of fishes and the ratio of fish biomass to lake volume.

The dominant form of phosphorus released through egestion and excretion

appears to be soluble reactive phosphorus (SRP). In a study of carp excretion, Lamarra (1975) found 50% of total phosphorus released to be SRP which would be available for algal uptake. Koonce and Seadler (unpublished manuscript) also reported that SRP was a significant fraction of the total phosphorus released. They found that the SRP fraction was consistently near 40% of the total phosphorus released. Detailed analysis of the molecular forms of the soluble organic fraction revealed a dominant high molecular weight fraction (>10,000 MW) and a low molecular weight fraction ($\sim$6,000 MW).

Temperature dependence of phosphorus release by fish has not been well studied. Koonce and Seadler (unpublished manuscript) observed that phosphorus release declined with decreasing temperature (25°C vs. 17°C), but that this relationship seemed to reflect the temperature dependence of consumption. In general, they found that the specific phosphorus release rate was a linear function of specific consumption rate. Efficiency of phosphorus assimilation may also vary with consumption rate. At low consumption rates, Koonce and Seadler found an assimilation efficiency of 33%, but the efficiency approached 80% at higher feeding rates. Nakashima (1980) found that at dietary P levels from 1.1-3.1 g P/100 g dry food, yellow perch maintained at similar rations (1.5% of body weight day^{-1}) and constant temperatures (12°-21°C) had relatively similar absorption efficiencies of 71.6 $\pm$ 7.2%.

In overview, carefully controlled and complete experimental determination of P excretion and egestion rates by fish remains uncompleted. Although of physiological interest, the rates reported to date are generally so low as to be of little ecological consequence (Kitchell *et al.* 1979, Nakashima 1980) except under the rare conditions of a large biomass of fish confined to a relatively small volume of water (Stanley 1974, Lamarra 1975).

STORAGE AND TRANSLOCATION OF PHOSPHORUS

The P content of fish biomass is generally 3-4% of dry weight; i.e. 3-4 times that of typical invertebrate prey. Because fishes are long-lived and have low rates of P turnover per unit mass, fishes can operate as a phosphorus sink. In shallow productive lakes, fish biomass can be the single largest pool of phosphorus in the limnetic zone. Kitchell *et al.* (1975) estimated Lake Wingra's fishes to contain 70% of the total pelagic P during summer months. Nakashima (1980) estimated the Lake Memphremagog fish populations to contain an amount of P approximately equal to that of the total sestonic P; i.e. 50% of total pelagic P. Lake morphology and productivity are obviously important determinants of the relative amount of P stored in fish biomass.

Migration, aggregation, and pulsed mortality of fishes followed by rapid decomposition can yield substantial local fertilization. Approximately 50% of the P stored in fish biomass, however, is apatitic and thereby refractory to decomposition (Smith *et al.* 1977). The most dramatic examples occur with anadromous fishes.

In summary, the effects of P storage and translocation by fish appear to be local and short-term. However, significant whole-system implications related to enhanced recruitment can result in greater densities of size-selective predators whose effects, as developed in the following section, can profoundly influence P cycling in subsequent years.

THE EFFECTS OF SIZE-SELECTIVE PREDATION

The greatest potential importance of fishes in phosphorus cycling is through their role as selective predators. There is substantial and diverse evidence of the significant effect of selective predation on planktonic systems (Hall et al. 1976, Porter 1977). Peters (1975) reviewed the importance of zooplankton body size in P cycling. The dramatic effects of predation on zooplankton assemblages have been demonstrated in systems ranging from small ponds to the largest of lakes (e.g. Wells 1970, McNaught and Scavia 1976).

Bartell and Kitchell (1978) estimated that P flux through an equivalent biomass of Lake Wingra zooplankton may have been increased by as much as 40 fold due to intensive size-selective predation. Enhanced productivity in European fish ponds is ascribed to the increased nutrient cycling rates effected through size-selective predation by cyprinid zooplanktivores (Wolny and Grygierek 1972). Shapiro et al. (1975) argued that predation by size-selective perch also enhances algal productivity but does so by effectively releasing phytoplankton from the grazing pressure of a large and abundant zooplankton assemblage. Thus, in some lakes, intense predation might reduce the rate of phosphorus recycling through reduction of zooplankton biomass.

Bartell (1978) also used Peters' (1975) model to estimate the impact on phosphorus excretion rates of selective predation by fishes in several lakes. Based on the data of Wells (1970), alewife reduced Lake Michigan zooplankton size and biomass to a level such that total phosphorus flux through zooplankton was reduced by about 50% during high (1966) versus low (1954) abundances of alewife. Less dramatic changes were estimated for other lakes (Hutchinson 1971); six of ten showed some potential increase in P flux due to reduced mean size of zooplankton which was not offset by equivalent reductions of biomass.

Bartell and Breck (1979) estimated from theoretical and experimental evidence that even whole-system P cycling rates might vary up to two fold due to the effects of selective predation. Although Nakashima (1980) discounted selective planktivory as important in Lake Memphremagog, his study did not consider planktivory by juvenile fishes nor the characteristics of P cycling in a system not continuously manipulated by fish predation.

Experimental studies conducted in microcosms provide further support of the important role of predation by fishes in phosphorus cycling. Hurlbert et al. (1972) chronicled dramatic changes in the nutrient status of systems manipulated by the addition of fish. Cooper (1973) demonstrated enhanced primary productivity at intermediate levels of grazing by a herbivorous fish. In general, any manipulation of zooplanktivorous fish populations will result in altered phosphorus cycling. The direction and magnitude of change will vary depending on the system, but will be most manifest in the epilimnion. The effect, however, can also extend to other subsystems (e.g., hypolimnion, littoral) due to the mobility of the consumers and the dynamics of water masses (Kitchell et al. 1979).

The critical unknowns revolve around a mechanistic description of selective predation processes appropriate to a specific trophic exchange (Vanderploeg and Scavia 1979) and some reasonable estimator(s) of potential biomass dynamics. Optical foraging theory provides a framework for the former (Werner 1977); the biota specific to a particular lake dimension the response surface.

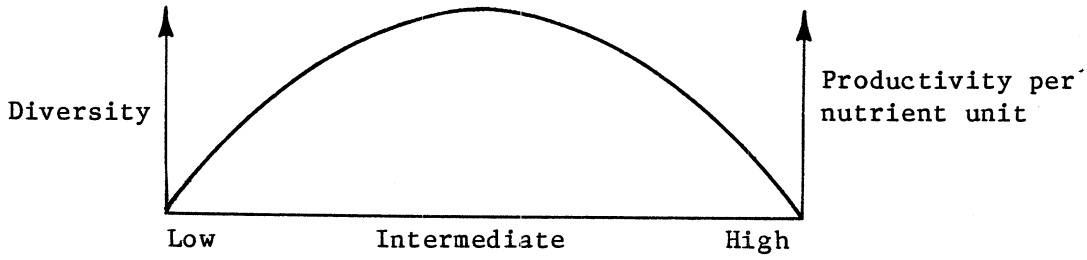
The documented selectivity of piscivores, including both other fishes and

man, can effectively structure fish populations and thereby alter abundances of the zooplanktivorous forms. The same need for mechanistic, predictive principles applies.

PREDATION, COMMUNITY STRUCTURE, AND NUTRIENT CYCLING

There exists a vast and growing literature, both theoretical and experimental, addressing the role of predation in resource utilization patterns and species packing in ecological communities. The mechanism(s), originally described by Paine (1966) as a "keystone" predator effect, have subsequently been elaborated, but the central theme remains -- predation can enhance prey diversity by selective reduction of superior competitors (e.g. recent review by Glasser 1979). Consequently, more prey species may coexist, allowing a greater diversity of life history stages and strategies to persist within a given habitat. The latter consequence has potentially important implications in epilmnetic environments where resource availability may stochastically vary. Inputs include allochthonous P loading from storm runoff or entrainment of hypolimnetic water masses. Continuous (but intermediate) levels of predation allow many species to coexist at population densities approximately optimal for sustained resource utilization with modest competition, yet at population densities sufficiently large to respond with minimal lag to pulsed increases in resource availability. Huston (1979) discussed the role of frequency of disturbance, competition, and predation in maintaining high diversity and highly productive populations under dynamic equilibrium conditions. This complexity of interacting mechanisms seems applicable at other levels of aquatic trophic exchange (e.g. McGowan and Walker 1979), as well as in terrestrial systems (McNaughton 1979) and aquatic systems (Cooper 1973, Porter 1977).

Huston (1979) argued that what had appeared as conflicting evidence (i.e. some studies demonstrating increased diversity as predation pressure increased, other studies demonstrating the reverse) simply represented either the ascending or descending limb of a total response that is unimodal. Diversity is enhanced at intermediate levels of predation, as represented in the sketch below:



The sketch also demonstrates a general relationship between predation intensity and productivity per unit of nutrient similar to that derived from experimental studies of algal production under varying intensities of grazing pressure by a herbivorous fish (Cooper 1973). The general response is the basic tenant of maximum sustained harvesting strategies developed for fisheries (Larkin 1978). However, the maximum yield is rarely sustained over long time periods due primarily to instabilities associated with stochastic effects on recruitment and the fact that fisheries like long-lived predators have substantial predatory inertia (Stewart et al. unpublished manuscript) relative to the dynamics of their prey.

The greatest positive feedback of nutrient cycling rates enhanced by selective predation occurs at intermediate levels of predation where highest diversity is maintained. The diverse forage base supports an equally diverse assemblage of foraging strategies. Populations are continually reduced by predation but to levels characterized by the log phase of rate of increase and rapid rates of turnover. Densities of various potential competitors are high enough to better withstand reductions through stochastic effects (Chesson 1978). Mean sizes of individuals are sufficiently large to maintain high reproductive potential yet generally much smaller than that for a dominant, senescent population. Accordingly, size-related nutrient feedback mechanisms operate at relatively high rates.

Lower predation rates result in lower diversity due to increased competitive exclusion. Dominant competitors develop large and more senescent populations; fewer life history strategies exist and fewer trophic linkages yield fewer alternative nutrient feedback pathways. Consequently, stochastic input may have a lower probability of enhancing some component of the community or, if a negative event, a higher probability of further reducing diversity.

Very intense levels of predation also result in lower productivity due to overexploitation. Primary prey species populations are depressed, and lags in the growth response result in less efficient utilization of pulsed resource availability. A higher probability of local extinctions due to stochastic events exists due to reduced specific population sizes (Chesson 1978).

The proposed relationship between productivity per unit nutrient and predation intensity varies with the annual cycle. Seasonal succession of planktonic forms results in rapidly changing optima confounded by the co-evolutionary history of organisms involved (Porter 1977, Kitchell et al. 1979). Moderate predation pressure should, however, moderate the succession rates through reduced competitive displacement. Integrated over an annual cycle, the cumulative effect should yield a greater total productivity and the highest efficiency of nutrient cycling. This general mechanism is offered as a hypothesis to be evaluated in modeling exercises and experimentation.

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CHAPTER VI

THE BIOLOGICAL COMPONENT OF PHOSPHORUS EXCHANGE AND CYCLING IN LAKE SEDIMENTS

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INTRODUCTION

The exchange and cycling of phosphorus between lake sediments and the overlying waters is a complex process that occurs in several stages: input via particulate deposition, biotic mineralization and diagenetic chemical transformation, release into the interstitial waters and, finally, release through the sediment-water interface. The rate at which each of these stages proceeds is dependent upon the interaction of numerous physical, chemical, and biological variables. This review will summarize what is known of the biological aspects of the regenerative process.

Most of what is known of the relationships between biotic activities and sediment P flux has been gained only in the past decade. The classical concept of sediment P exchange viewed the sediments as a sink; release of P into the overlying waters only occurred during periods of low oxygen concentrations, as in the hypolimnion of eutrophic lakes during summer stagnation, and was intimately related to the chemical kinetics of iron phosphate compounds (Mortimer 1941, 1942; Hayes et al. 1952; Stumm and Leckie 1971). Recent evidence, however, indicates that P release also occurs when dissolved oxygen concentrations are high. Although release under aerobic conditions is about ten times less than under anaerobic conditions (Burns and Ross 1972, Holdren and Armstrong 1980), the significance of aerobic P release should not be minimized. In the Great Lakes, Mortimer (1971) predicted that significant P release would only occur when oxygen concentrations were below 2 mg/L, and Burns and Ross (1972) found anoxic regeneration of P in central Lake Erie only when oxygen concentrations were below .6 mg/L. Such low oxygen levels are found only in a limited area of the Great Lakes. Aerobic conditions exist throughout the nearshore area and sediment P release here would be well-circulated and available for algal uptake. Under some conditions, as shown by experiments on deepwater Lake Ontario sediments, aerobic release may even equal anaerobic release (Bannerman et al. 1975).

The exact mechanisms of aerobic P release are virtually unknown, but appear related to the activities of benthic organisms. Wood (1975) suggested that, of several mechanisms responsible for materials movement across the sediment-water interface, ordinary diffusion was the least important while biotic activities were of considerable importance. Holdren and Armstrong (1980) found that, of the factors they investigated, the presence of benthic organisms had the greatest effect on sediment P release rates. Lee et al. (1977) attributed aerobic P release to the microbial mineralization of P compounds.

Traditionally, benthic organisms can be divided into several categories based on relative size: the macro-, meio-, and microbenthos. In the Great Lakes, typical representatives of each of these categories are oligochaetes, Pontoporeia, chironomids, and pelecypods (macrobenthos); nematodes, cladocerans, and copepods (meiobenthos); bacteria and algae (microbenthos). The biotic activities of each of these benthic groups affect the uptake and release of sediment P, and although each activity mediates sediment P in a unique way, each is intimately related to the activities of the other groups. The biotic role can be broadly defined by the following activities: bioturbation, uptake and excretion, and organic mineralization.

MACROBENTHOS AND BIOTURBATION

Bioturbation is the mechanical mixing of the sediments by the burrowing and feeding activities of the benthos. Though meio- and microbenthos may have some role in bioturbation, most of the actual mixing process is a function of the macrobenthos, particularly those taxa with body dimensions greatly exceeding the sizes of the sediment particles. Such stirring activities lead to both physical and chemical changes that alter exchange processes. Bioturbation increases mixing and exchange of interstial water, facilitates the import of oxygen, affects Eh and pH profiles, and alters sediment structure. These changes, in turn, affect the rate of phosphorus release either by increasing exchange along concentration gradients or by changing the solubility of phosphorus compounds.

Modes of bioturbation are species specific. The impact of a particular species depends on its size, feeding system, and depth of penetration. In the nearshore Great Lakes, the most abundant macrobenthic forms are the oligochaete worms, especially in enriched areas. These deposit-feeders typically ingest sediments below the surface (2-5 cm), then defecate at the sediment-water interface. Thus, large volumes are moved upward, effectively "recycling" buried deposits for further aerobic mineralization and nutrient release and absorption of new materials. The fecal material differs in its chemistry and structure from the underlying sediments in ways that enhance microbial growth and mineralization (Brinkhurst 1972). Mixing of the upper sediments is complete, as evidenced by experiments using radioactive tracers (Robbins *et al.* 1977) and pollen grains (Davis 1974a). The amount of sediment reworked can be put in perspective by comparing it to rates of deposition. In the profundal of Lake Huron, the annual amount of sediment reworked by the lumbriculid oligochaete *Stylodrilus heringianus* in the upper 3 cm of sediment was four times greater than the annual sedimentation rate (Krezoski *et al.* 1978), and in western Lake Erie the amount reworked by tubificid oligochaetes was ten times greater (Fisher 1979). Under optimum conditions and at densities found in some areas of the Great Lakes, laboratory experiments have shown that tubificids are capable of reworking the top 5 cm of sediment every 2 weeks (McCall and Fisher 1977).

The physical effects of sediment reworking by oligochaetes can be profound. McCall and Fisher (1980) found that virtually all sediment properties that they examined - sediment grain size, settling velocity, erodibility, porosity, and permeability - were altered by factors of at least two to sometimes ten or more by the presence of tubificids. The continuous deposition of fecal material at the sediment surface produces an uncompacted layer that is easily resuspended by bottom currents. The implication of these activities would be greatest in the nearshore where the extent of wind-generated sediment transport and the physical regeneration of P have been aptly demonstrated by Lam and Jaquet (1976).

Besides altering the character of the sediments by their burrowing and feeding, tubificids actively pump water through their burrows, as related to respiratory requirements. Although such activity does not represent bioturbation in the strict sense, these movements increase exchange between nutrient-rich interstitial waters and the overlying waters, leading to increased diffusion along concentration gradients. In polluted Toronto Harbour, which has an extremely high tubificid density, the amount of water circulated through the sediments was estimated at between 184 and 291 mL m^{-2} hr^{-1} (Wood 1975).

In the offshore waters of the Great Lakes, the dominant organism is Pontoporeia hoyi. This amphipod randomly burrows in the top 1-2 cm of sediment and makes brief excursions into the overlying waters. These activities resuspend sediment particles and prompted Robbins et al. (1979) to model them as an "eddy diffusion" process. In the Baltic, a highly turbid zone extending above the bottom has been observed in areas with high densities of Pontoporeia affinis (Ankar 1977). The effect of this sediment mixing on phosphorus flux can be derived from laboratory experiments; sediment agitation has consistently led to increased phosphorus release.

Other macrobenthic components include chironomids and pelecypods. Many species of the former group build vertical burrows extending from the sediment surface to a depth of 2-3 cm. While these larvae do not continually move particles as do the tubificids, they pump more water through the sediments since circulation is required for both feeding and respiration. Tessenow (1964) reported that chironomids created oxidized mud tubes to a depth of 10 cm (most species probably affect only the top few cm) and that this activity greatly increased the release of dissolved silica. In addition, the emergence of adult chironomids has an immediate and pronounced effect on nutrient release rates when densities are high (Holdren and Armstrong 1980). Sphaeriids (fingernail clams) are found throughout the Great Lakes, sometimes in great abundance. Although surface dwellers, they are capable of extending their foot 2.5 cm into the sediments. McCall et al. (1979), in a series of laboratory experiments, found that a large pelecypod species, commonly found in western Lake Erie, significantly altered sediment porosity and induced incomplete sediment mixing down to 20 cm.

MACROBENTHOS AND P EXCRETION

The extent to which the macrobenthos mediate nutrient exchange through digestive processes is not well-defined. Although the excretion rate of phosphorus by zooplankton is well documented (See Chapter IV), studies to determine the excretion rate of benthic invertebrates are few and limited to large marine species (Johannes 1964a, Kuenzler 1961). The potential impact of organisms converting organically bound phosphorus to more soluble forms and depositing particulate phosphorus via faecal pellets can be substantial. This is true especially for deposit feeders, considering the high rate at which material is passed through their gut. For instance, Brinkhurst (1972) estimated that, of 833 tons of nitrogen entering Toronto Harbour each year, 113 tons circulated through the tubificid population alone.

In studies where sediment phosphorus release is directly attributed to faunal activities, it has not be determined whether the release resulted from bioturbation or excretion (Graneli 1979, Gallepp 1979, Holdren and Armstrong 1980). However, Gallepp (1979), using a regression equation relating dry weight to P excretion developed from marine species (Johannes 1964b), estimated that chironomids could account for all the phosphorus released during the course of his experiments.

MACROBENTHOS AND SEDIMENT P RELEASE

In experiments specifically designed to measure the impact of macrobenthic activities on sediment P flux under aerobic conditions (paired comparisons with and without organisms), the organisms either decreased P in the overlying waters (Davis et al. 1975), caused no change (McCall and Fisher 1980), or increased it (Gallepp 1979, Graneli 1979, Holdren and Armstrong 1980). When organisms did increase phosphorus release, the increase over background levels was quite variable (Table 1). These results do not indicate inconsistencies in macrobenthic activity, but reflect the complexity of sediment P dynamics. P is present in lake sediments as organic, absorbed, iron-, aluminum-, and calcium-bound phosphates. The proportion of P available for release depends on the compounds present and on the kinetics of such chemical exchange reactions as acid-base, precipitation, complexation, oxidation-reduction, and sorption (Lee 1970). Since most of these reactions are complex functions of Eh and pH, P compounds can be divided into two categories, redox-sensitive or redox-insensitive (Davis et al. 1975). For example, while insoluble Fe (III) P is reduced to soluble Fe (II) P under low oxygen conditions and suitable pH (redox-sensitive), ion exchange of P between the sediments and water is not responsive to Eh changes (redox-insensitive). Bioturbation increases sediment Eh, which results in a net uptake by the sediments if most P is redox sensitive, but it also increases interstitial and overlying water exchange, which results in a net release by the sediments if most P is redox-insensitive or a result of biotic mineralization and excretion. However, if faunal activities lead to sediment P release, it does not necessarily follow that redox-sensitive P is not involved. The amount of redox-sensitive P that is fixed or released is a function of sediment composition. Since the binding capacity of redox-sensitive compounds is decreased at high pH levels, increases in sediment Eh would be less important in calcareous sediments. Both Graneli (1979) and Holdren and Armstrong (1980) found that chironomid activities increased P release to a greater extent in calcium-rich deposits.

In general, it seems that increased Eh as a result of bioturbation is not as important in binding P as increased water exchange is in releasing it. Williams and Mayer (1972) questioned the effectiveness of the oxidized microzone as a barrier to P release when it is unconsolidated and has a high water content. It is interesting to note that all studies with chironomids have shown an increase in sediment P release, while all studies with tubificids have shown a net uptake of P by the sediments (Davis et al. 1975) or no change (McCall and Fisher 1980), even though both chironomids and tubificids increase the import of oxygen and alter Eh and pH profiles (Edwards 1958, Schumacher 1963, Hargrave 1972, Davis 1974b, McLachlan and McLachlan 1976). This may be a result of the fact that chironomids probably pump more water through the sediments than do tubificids.

MEIOBENTHOS

Very little is known of the role of the meiobenthos in nutrient regenerative processes. This is particularly true in the Great Lakes where only one study (Nalepa and Quigley 1980) has quantified these forms. Because of their relatively small size and body mass when compared to the macrofauna, the ability of meiobenthos to cause significant changes in sediment character

TABLE 1. Release rates of phosphorus with and without organisms.

Location	Sediment P Release ($mg/m^2/day$) Without Organisms	With Organisms	Organism[1] Density (m^{-2})	Type of P Measured	Reference
L. Trummen	0.30	0.58	1,064	TP	Graneli (1979)
L. Arungen	0.95	1.98	1,064	TP	Graneli (1979)
L. Vombsjon	2.58	11.44	1,064	TP	Graneli (1979)
L. Mendota	0.30	9.40	6,585	TP	Gallepp (1979)
L. Mendota	0.10	7.70	6,585	SRP	Gallepp (1979)
L. Mendota	0.72	25.00	"high numbers"	DRP	Holdren and Armstrong (1980)

[1] All studies with chironomids. The Holdren and Armstrong (1980) study includes tubificids.

(bioturbation) has been considered slight. However, bioturbation (and excretion) can be potentially important because of their high metabolic rates and great densities. In the only study to document bioturbation by the meiobenthos, nematodes and associated fauna developed an oxidized surface layer .5-1.5 cm thick in anoxic sediments within a few hours (Cullen 1973). Unlike the macrofauna, nematodes are able to tolerate, even thrive, under anoxic conditions (Ott and Schiemer 1973). Considering the importance of anaerobic chemical processes in sediment P release, the impact of nematode activities under such conditions can be significant.

There is evidence that the meiofauna, particularly nematodes, are important in enhancing the mineralization of organic detritus by bacteria. In laboratory experiments, the mineralization rate of detritus in microcosms with macrobenthic detritivores and nematodes was twice that of microcosms with macrobenthic detritivores alone (Lee et al. 1975, Tenore et al. 1977). Interestingly, the presence of nematodes also increased the net incorporation of detritus by the macrobenthic detritivores.

Many species of meiofauna, e.g. copepods and cladocerans, freely enter the sediments from the water-column, particularly in response to diurnal light changes. At times, "planktonic" forms are more abundant in the sediments than in the overlying waters (Nalepa and Quigley unpub. data). Wetzel (1975) suggested that these sediment excursions are for feeding purposes. In addition, many benthic taxa enter the water column (Wiley and Mozley 1978). Frequent movement of organisms across the sediment-water interface may represent an additional pathway for nutrient release -- uptake in the sediments followed by release (excretion) in the water column. The impact of these activities would be greatest in the nearshore area where the water volume to sediment ratio is small, and the density of organisms per unit volume is high.

MICROBENTHOS

Bacteria play a diverse role in sediment-nutrient flux. In addition to influencing the solubility of P compounds with their metabolic end products, bacteria form an important link between the nutrients locked in detritus and the nutrient uptake and release by the macro- and meiobenthos. It is generally recognized that the bacteria are responsible for most, if not all, mineralized organic input. They are capable of assimilating a variety of organic compounds which other heterotrophs cannot utilize (Nielson 1962). Since bacteria, in turn, are utilized as a food source by other benthic forms, they represent perhaps the most important link in the cycling of sediment nutrients.

The bacteria-benthic fauna association and its implications to nutrient flux are more complex than a simple food-chain interaction. Macro- and meiofaunal activities benefit bacteria growth and, thus, stimulate organic decomposition by (1) improving the import of oxygen, (2) breaking down larger particles, thereby improving the substrate for colonization, and (3) feeding on bacteria and keeping them from reaching self-limiting numbers. Laboratory experiments consistently indicate improved bacterial activities in the presence of faunal grazers (Hargrave 1970, Fenchel 1972, Lopez et al. 1977, Lee et al. 1975, Tenore et al. 1977). Zvetkova (1972) noted that the rate of biochemical oxidation of organic matter increased 1.5 to 2 times in the presence of tubificids. Provini and Marchetti (1976) found that the total oxygen consumption of sediments was seven times greater than the sum of the oxygen

uptake of sediments and tubificids measured separately. This difference was attributed to the increased microbial activity resulting from sediment irrigation and uplifting by the tubificids.

Tubificids (and probably other Great Lakes benthic groups as well) have a remarkable preference for special bacteria groups and possess the ability to detect and discriminate them among others (Brinkhurst and Chua 1969, Wavre and Brinkhurst 1971, Chua and Brinkhurst 1973). How this selective feeding affects the rate of organic decomposition is unknown.

When sedimented organic material is mineralized, a portion is returned in soluble form to the overlying waters, and part remains in the sediment. Burns and Ross (1972) estimated that in Lake Erie, under aerobic conditions, 25% of sedimented P is returned to the water column and 75% remains complexed in the sediments. The sediment P either accumulates and is held by bacteria, or is absorbed on the sediments. Pomeroy et al. (1965) found that both of these pools are involved in equilibrium exchanges. In undisturbed sediments, most of the P exchange is a physical sorption reaction; bacteria beneath the sediment-water interface also exchange P, but the exchange is with the interstitial waters which, in turn, only slowly diffuse upward. When the sediments are disturbed (as during bioturbation) or scoured, bacterial P freely exchanges with the overlying waters.

During long-term laboratory experiments, the addition of antibiotics to inhibit bacteria has caused either a net increase (sediment desorption) (Kamp-Neilson 1974), no change (Pomeroy et al. 1965, Fillos 1977), or a net decrease (sediment sorption) (Hayes and Phillips 1958) of P into the overlying waters. Such variable results are not surprising considering the multitude of factors that can potentially affect P release, i.e. binding capacity of sediments, concentration gradients, degree of sediment disturbance, etc. It is unfortunate that none of these studies documented faunal densities.

Epipelic algal communities of the sediment-water interface may provide a driving force for more rapid flux of nutrients (Lee 1970). The flux may stimulate planktonic algal growth, a well documented phenomenon (Gahler 1969; Golterman et al. 1969; Fitzgerald 1970a, 1970b; Porcella et al. 1976). For laboratory algal culture studies in which calcium hydroxyapatite was used as the phosphorus source, the algae acted as a "sink" by driving reactions in the direction of material transfer from apatite to the organism (Gerhold and Thompson 1969). Williams et al. (1980) reported that P uptake by algae was related to the amount of nonapatite inorganic P in the sediments. Ripl and Lindmark (1979) demonstrated that P supplies within laboratory cultures of Selenstrum capricornatum were controlled partially by both sediments and algal abundance. Phosphorus release from the sediment was enhanced when algae were present, and it was concluded that mutual interactions between algae and bacteria largely control the form of nutrient release. Porcella et al. (1970) noted that the relative abilities of different sediment types to support algal growth were related to the amount of available phosphorus in the sediments. Further, physical and chemical fluctuations induced by algal populations appeared to directly affect phosphorus flux from the sediments. In the Porcella et al. (1970) study, the development of a thick mat of Oscillatoria on the sediment resulted in (1) the development of anaerobic conditions, (2) the disruption of mixing with overlying waters, (3) a higher transfer rate of phosphorus from the sediments, and (4) the providing of a source of organic materials (secreted by the algal cells) which served as a substrate for other organisms. The role of algae actually occurring in the sediments (epipelic types, primarily diatoms) in phosphorus cycling is unknown.

FISH

Although not part of the benthos in the strict sense, bottom-feeding fish influence sediment P release by stirring the sediments and selectively preying on benthic forms. Grygierek et al. (1966) reported that blooms of various phytoplankton species tend to last longer when bottom-feeding fish are present. Hrbacek et al. (1961) noted that fish removal from a lake caused a decrease in chlorophyll concentration. Needham (1966) similarly observed that the Chlorophyta decreased steadily after the removal of bottom-feeding fish. Kitchell et al. (1975) concluded that bottom-feeding fish excreting relatively low but constant levels of phosphorus may act to stabilize planktonic communities which would otherwise exhaust available phosphorus. Likewise, Lamarra (1975) viewed the digestive activities of carp (Cyprinus carpio) as a major contributor to the nutrient loading of lakes. Although fish excrete phosphorus, they probably have a greater impact on the phosphorus cycle by structuring the benthic community through selective predation (Bartell and Kitchell 1978).

BENTHOS-SEDIMENT INTERACTIONS IN NUTRIENT CYCLING MODELS

In spite of the evidence that benthic animal activities affect nutrient exchange processes, few models account for the consequences of these activities. Berner (1977) avoided modeling exchange processes in the top 10-20 cm of sediments where animal activities were most prevalent, and Vanderborght et al. (1977a, 1977b) chose to model processes in areas having high surface currents and correspondingly low animal densities. Such reluctance to include biotic components in modeling efforts is due to an appreciation of the important role of the benthos in sediment-water exchange processes and the lack of detailed information at hand. To date, one group of researchers (Goldhaber et al. 1977) included the effects of bioturbation in a steady-state diagenetic model of sulfate reduction and diffusion. Similarly, the inclusion of animal activities will lead to more reliable models of nutrient cycling in the Great Lakes.

SUMMARY

The importance of benthic organisms in the cycling and exchange of phosphorus and other nutrients between sediments and overlying water has only been recognized in the past decade. Recent evidence indicates that aerobic sediments are not a complete sink for phosphorus, and that more phosphorus is regenerated than can be accounted for by diffusive processes alone. The relationship between the biotic component and sediment phosphorus flux is complex, partly as a result of the functional interactions between the various benthic organisms, and partly as a result of the complexity of sediment phosphorus kinetics.

At this point, three major functions of the benthos in phosphorus cycling and regeneration have been defined. The first, bioturbation, or the physical mixing of sediment by the larger organisms, leads to changes in porosity, increases interstitial water and oxygen exchange, and alters Eh and pH profiles. In turn, these changes may alter phosphorus cycles, depending on the

forms of phosphorus present and the physical and chemical character of the sediment. Both oligochaetes and chironomids play a major role in this process. Second, such biological activities as ingestion, assimilation, and excretion transform phosphorus compounds; however, actual measurements of P flux as a result of these activities are non-existent. The third function of benthos is the mineralization of organic compounds and the subsequent release of P.

Laboratory experiments sepcifically designed to determine the impact of organism activities on sediment P flux, e.g. comparisons with and without organisms, have given conflicting results and are an indication of the number of variables that can potentially alter exchange processes.

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CHAPTER VII

THE ROLE OF MACROPHYTES IN PHOSPHORUS CYCLING

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INTRODUCTION

One of the characteristics of the littoral zone of lakes is the growth of aquatic macrophytes. The littoral zone, in relation to the size of the pelagic region, varies greatly among lakes depending on the geomorphology of the basin. Because the littoral zone intercepts both the terrestrial and aquatic systems, its chemical and biological features are inherently influenced by both systems. Rich nutrients received from the drainage basin often contribute to intensive biological activity. Littoral flora constitute the major source of synthesis of organic materials that regulate the biological productivity and metabolism in the littoral zone.

Aquatic macrophytes constitute the macroscopic forms of aquatic vegetation including macroalgae, pteridophytes (mosses and ferns), and the angiosperms (flowering plants). According to their growth forms, aquatic macrophytes can be differentiated into submergents, emergents, and free floaters. The biology of aquatic macrophytes has been a subject of many investigations and reviewed in great detail by Gessner (1959), Sculthorpe (1967), and Hutchinson (1975). One of the most significant roles of aquatic macrophytes in the aquatic ecosystem is their involvement in the nutrient cycling in the littoral zone.

PHOSPHORUS CONTENT IN AQUATIC MACROPHYTES

The content of P in aquatic macrophytes varies widely depending on the species, growth cycle of plants, and availability of the nutrient in the growth medium. To evaluate the nutrient status of the aquatic vegetation, the tissue analysis technique was introduced to establish the critical, deficient, and luxury concentrations of nutrient (Gerloff and Krombholz 1966, Fitzgerald 1972). Tissue analysis requires establishing the critical concentration of P or other elements of interest for each species: that concentration is the minimum level for maximum growth. Below this level is the deficient zone in which the plant yield is proportional to its P content. Above this level is the zone of luxury consumption in which the P content in the organism increases but the growth does not. The status of element content in the plant indicates the nutrient availability in the growth media.

In experiments with several species of aquatic plants, Gerloff and Krombholz (1966) concluded that the critical P level of 0.13% was applicable to aquatic vegetation in Wisconsin lakes. Moreover, they reported that the aquatic macrophytes in eutrophic and mesotrophic lakes in Wisconsin contained P above the critical value and those in oligotrophic water below that value. The P content, however, may change considerably during the growth season (Adams and McCracken 1974). Reimer and Toth (1968) analyzed vegetative parts of 37 species of aquatic plants and found that the P content ranged from 0.1 to 1.95%, with a mean of 0.45%. Bernatowicz (1969), however, reported a lower range (0.01-0.61%, with a mean of 0.17%) of P from 16 species.

UPTAKE AND RELEASE OF P

The uptake and release of P by aquatic macrophytes have been a subject of numerous studies (e.g., Gerloff 1969, Fitzgerald 1972, McRoy and Barsdate 1970, Denny 1972, McRoy *et al.* 1972, DeMorte and Hartman 1974, Peverly and Brittain

1978). It is a well-known phenomenon that the submerged macrophytes can absorb P by the shoot-foliage portion from the water and by the root-rhizome system from the substratum. The efficiencies of P uptake by those two portions of plants are quite variable among species (Sculthorpe 1967).

In addition to active excretion of P by living macrophytes, leaching from dead biomass is rapid. Even under sterile conditions a loss of from 20 to 50% of total P may occur in a few hours. Phosphorus released from decaying macrophytes is mineralized quickly, being either rapidly utilized by bacterial and algal populations or incorporated into the sediments (Nichols and Keeney 1973).

The dynamics of phosphorus cycling in relation to littoral vegetation was repeatedly demonstrated earlier using radioactive ^{32}p (e.g. Hutchinson and Bowen 1947, 1950; Coffin et al. 1949; Hayes et al. 1952; Hayes and Phillips 1958). Their results indicated that the P added to the surface water was rapidly absorbed by littoral vegetation and phytoplankton. Consequently the P was slowly released to the surrounding water by the plants and rapidly released by the epipelic algae on the plants.

PHOSPHORUS IN GREAT LAKES MACROALGAE

The distribution of aquatic macrophytes in the Great Lakes littoral zone is relatively limited, and their role in nutrient cycling in the whole lake system appears insignificant. Certain species of filamentous algae, however, are common to the lower Great Lakes, and excessive growth of these algae often occurs in nutrient-rich water. Cladophora glomerata, a highly branched green alga, constitutes the most important aquatic macrophyte in many areas of the Great Lakes littoral region (International Joint Commission 1975), particularly in western Lake Erie (Taft and Kishler 1973), the southern shore of Lake Ontario (Wezernak et al. 1974), and the southwestern portion of Lake Michigan (Herbst 1969, Lin and Blum 1973). The most comprehensive information on Cladophora distribution is available for Lake Ontario. In western Lake Ontario, the Cladophora growth was estimated to occupy an area of 2,300 acres within 3-meter contour between Toronto and Hamilton. From Rochester east to Stony Point, Cladophora covers 79% of the bottom in a band 350-m wide. In Lake Erie, the dense Cladophora growth occurs on the southern shore of the eastern basin where a 35 mi^2 growth bed was estimated. The total area of Cladophora growth on the U.S. shore of Lake Erie was estimated at 350 mi^2 (International Joint Commission 1975). The average Cladophora biomass from samples collected in Lake Ontario was 168 g/m^2 dry wt and in Lake Erie was 100 g/m^2 (see Neil 1974). The extensive Cladophora occurrence in those areas may have a significant impact of P cycling in those littoral zones. In general, the distribution of Cladophora in the lower Great Lakes is primarily limited by light, substrate availability, and nutrient level in the lake water.

Nutrient supplies and limiting nutrients for Cladophora growth in the Great Lakes have been the subjects of many investigations (Neil and Owen 1964; Herbst 1969; Fitzgerald 1970; Lin 1971,1977; Taft and Kischler 1973; and Gerloff and Fitzgerald 1976). Extensive growth of Cladophora usually occurs in the areas receiving nutrients from municipal waste water discharges which contain a high concentration of P. Although the growth rate and distribution of Cladophora have been shown to be closely related to phosphorus inputs, the key phenomenon of phosphorus uptake kinetics in relation to growth rate is not

well known. It is well documented that Cladophora can take up P from an external source and build up an internal pool as a result of luxury uptake (Gerloff and Fitzgerald 1976, Lin 1977). Recently, Auer and Canale (1980) observed that internal P pools may regulate the uptake of P through a saturation feedback mechanism, i.e. the apparent maximum P uptake rate decreases with increasing internal pool size. Under P-limiting conditions, the P uptake rate increases with increasing external P concentration. While the P uptake kinetics are expected to follow a hyperbolic function, the saturation concentration for uptake is often greater than the P value observed in natural systems. Compared to planktonic algae, Cladophora has been shown to have certain disadvantages in P uptake. For example, its half saturation constant is much greater than that of planktonic algae, and the maximum P uptake rate (on dry weight biomass basis) is much smaller than that measured for several species of phytoplankton.

The critical cellular P concentration required for maximum growth of Cladophora is 0.06% of dry weight (Gerloff and Fitzgerald 1976). This value is relatively lower than that of other aquatic macrophytes (Gerloff and Krombholz 1966). Gerloff and Fitzgerald (1976) also showed that samples of Cladophora collected from all the Great Lakes except Lake Superior contain P concentrations ranging from 0.07 to 0.82%, indicating that most of the Cladophora growth in the Great Lakes is P sufficient. Unlike rooted aquatic macrophytes that can absorb their phosphorus from the substrate by root systems (Carignan and Kalff 1980), Cladophora must obtain its nutrient from surrounding water through the filaments. Since this alga normally occurs in a shallow littoral region where sediment resuspension prevails, it may be able to use condensed P originated from sediments. Lin (1977) reported that Cladophora could utilize pyro- and tripoly-phosphate efficiently because the algae can enzymatically hydrolyze condensed P on the cell surface and extracellularly.

In regard to the efflux of P in Cladophora, Auer and Canale (1980) observed that algae excrete P when cells with high internal P pools are placed in a low P environment. Furthermore, they showed that the half-saturation constant for P excretion is approximately 20% of the maximum pool size. In addition to P release by live cells, the nutrient regeneration through the decay of Cladophora biomass is expected to be a significant process in which a massive quantity of this alga periodically becomes detached from its substrate. Unfortunately, very little investigation has been done on P release from Cladophora and its effect on nutrient cycling in the Great Lakes littoral zones where this alga is an important vegetation.

Besides Cladophora, other filamentous macroalgae common to the Great Lakes are Bangia atropurpurea and Ulothrix zonata. Although they seldom develop to significant standing crops, the recent invasion of Bangia in the Great Lakes (Lin and Blum 1977) may have indicated a threshold change in certain nutrient regimes in Great Lakes water. Nutrient requirements for these algae remain uninvestigated.

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CHAPTER VIII

CONCEPTUAL MODEL OF PHOSPHORUS CYCLING

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INTRODUCTION

There presently exists a broad spectrum of models addressing phosphorus in lake ecosystems. These models range from relatively simple, empirical models of annual, lake-wide average total phosphorus concentration to more detailed seasonal, spatially segmented models describing dynamic interactions among many phosphorus components. Some models deal directly and solely with phosphorus while others track phosphorus stoichiometrically with carbon or other biomass variables. The motivation behind the different types of models also varies. Models with simple physical segmentation and few ecosystem compartments have been developed primarily for assisting water quality management, whereas other models, which include detailed segmentation and many compartments, have been developed generally for increasing our understanding of structure and function within the ecosystem. The purpose of this chapter is to briefly outline several categories of existing models and to construct a conceptual model useful for synthesizing and analyzing existing information on phosphorus cycling in lakes.

PREVIOUS MODELS

Management Models

The first category of models includes those designed around the phosphorus loading concept. A thorough historical review and quantitative critical valuation of these models is provided by Reckhow (1979). The development and refinement of the mass-balance-based phosphorus model for lakes is attributed to Vollenweider (1964, 1969) with significant alterations and improvements by Dillon and Rigler (1974) and Chapra (1975, 1977). These models are simply balances of phosphorus inflow, outflow, and sedimentation; the latter process is used to calculate the retention coefficient (R) for phosphorus. Expressions used for calculation of R have been examined statistically on several different data sets (Dillon and Rigler 1975, Vollenweider 1975, Kirchner and Dillon 1975, Chapra 1975, Larsen and Mercier 1975). Also, Reckhow (1977, 1979) and Walker (1977) evaluated overall model accuracy for this set of models using first-order error analysis. Modifications of the model have included sediment interactions (Lorenzen *et al.* 1976) and separation of epilimnion/hypolimnion and particulate/dissolved phosphorus compartments (Snodgrass and O'Melia 1975).

Although these models represent the only phosphorus-related models that have undergone extensive statistical evaluation with respect to general applicability across a wide range of lakes, they do not reveal much of the structure or function of the ecosystems. This black-box, mass-balance approach intentionally removes the effects of internal system dynamics. The models are designed specifically to assess whole lake trophic status (phosphorus and chlorophyll content) with respect to past, present, and expected phosphorus loads which reduces their effectiveness for examination of process-oriented cycling of phosphorus.

Eutrophication Models

A second category of models falls between the two extremes outlined above (management and ecosystem dynamics). These models, here termed eutrophication models, are concerned with simulation and prediction of seasonal phytoplankton biomass dynamics. This type of model, based on the early work of Riley et al. (1949), was reintroduced in the early 1970s (e.g. Chen 1970, DiToro et al. 1971) and has had several significant alterations and applications (e.g. Thomann et al. 1975, Chen and Orlob 1975, DiToro et al. 1975, DiToro and Matystik 1980).

These models focus on one or two groups of phytoplankton and use chlorophyll or dry weight as biomass indicators. A guiding principle behind development and tests of these models is that ecosystem processes will be included in the model only if they have significant impact on simulation and prediction of these crude indicators of phytoplankton biomass. Consequently processes such as phytoplankton production, respiration, and sinking; zooplankton grazing, respiration, and excretion; and crude cycles of phosphorus (two compartments) and nitrogen (three compartments) have been included. Properties and processes such as internal storage of excess nutrients by phytoplankton, minimum threshold of food for zooplankton grazing, multiclass descriptions of phytoplankton and zooplankton, and food-supply control of zooplankton respiration have not been included.

For phosphorus, the eutrophication models generally track the following classes: 1) available phosphorus, 2) non-living unavailable phosphorus, and 3) living plankton phosphorus. The last class of phosphorus is usually followed stoichiometrically with other biomass indicators (chlorophyll, carbon, dry weight). The models are not designed to follow details of the phosphorus cycle. Model component definitions are often operational and tied to their utilization by phytoplankton. Although this class of models has provided important advances in the use of more mechanistic models in management of aquatic resources, they too fall short of providing the detail and focus necessary to explore phosphorus cycling quantitatively.

Ecosystem Models

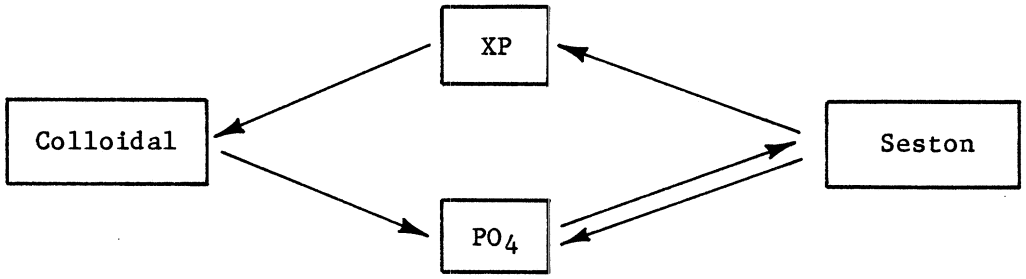
This class of models, although fundamentally similar to the eutrophication models, places emphasis on more detailed aspects of ecosystem dynamics. These models are oriented toward synthesizing existing information, simulating known conditions, and analyzing controls of system structure and function. Some models of this type have been used for prediction, however their applicability has not been tested as rigorously as the two other classes of models.

Ecosystem models emphasize more detailed aspects of plankton dynamics than do eutrophication models. For example, seasonal succession (e.g. Lehman et al. 1975, Bierman 1976, Scavia 1980), internal stores of nutrients (Lehman et al. 1975, Bierman 1976), size-selective, minimum-threshold zooplankton grazing (Scavia 1980), sediment-water column interactions (Larsen and Mercier 1975, Scavia 1980), bacteria dynamics (Bloomfield 1975, DePinto 1979), zooplankton vertical migration (Steele and Mullin 1977), and population structure (Steele and Frost 1977) have been included in several ecosystem models. Scavia (1979) provided a review of several detailed process components included in lake ecosystem models.

Ecosystem models are collections of formalized theories of process dynamics and are useful for describing and analyzing detailed aspects of the phosphorus cycle. One shortcoming is that they presently emphasize phosphorus dynamics only as they are directly related to plankton nutrition. The omission of detailed dynamics for nonliving phosphorus components reflects both the orientation of these models and the lack of information presently available on those components.

Phosphorus-based Ecosystem Models

Recently, models focusing on phosphorus as a system tracer have been developed. The models, most notably Lean (1973a), are based on radiotracer experiments and generally assume linear, steady-state kinetics. A variety of studies and experiments (Lean 1973a, b) have led to the following conceptual model:



where XP represents phosphorus compounds of relatively low molecular weight (250 MW), colloidal P represents relatively high molecular weight (>5,000,00 MW) compounds, PO_4 is dissolved orthophosphate, and seston is phosphorus associated with particles retained on a membrane filter with 0.45 μm pore size. Experimental work (Lean 1973a, 1973b; Lean and Rigler 1974, Lean and Nalewajko 1976, Paerl and Lean 1976) also has led to the following information: 1) Transfer from PO_4 through XP to colloid requires the presence of seston, indicating XP is excreted or otherwise released by plankton; 2) The pathway XP -> Colloid -> PO_4 is probably an exchange process of XP for PO_4 associated with the colloids, PO_4 is not adsorbed to the colloids; 3) Time-course studies showed decomposition of XP to PO_4 in 4 hr in a sterile environment, indicating the chemical instability of XP ($\sim$250 MW) compounds; 4) Kinetics of exchange with seston P indicate at least two seston compartments - a fast exchanger and a slow exchanger.

Phosphorus-based models provide important first steps in identifying significant nonliving phosphorus components and major pathways of phosphorus flow under steady-state, experimental conditions. However, because of their steady-state orientation, they do not provide theory for, nor tests of, hypotheses regarding seasonal, dynamic interactions among phosphorus components. Also, they are not oriented toward food-web dynamics and consider only radioactive labeled compounds over a relatively short time interval.

The above brief descriptions of extant modeling capabilities indicate that, while each class of models has attributes specific for its intended use, they all are incomplete with regard to examination of detailed phosphorus cycling for two reasons. Firstly, they generally do not follow many of the important components of phosphorus. The first class follows only total phosphorus and the other two classes follow only components directly related to

phytoplankton nutrition. The keys to many unresolved questions relating to utilization, cycling, and biological availability of phosphorus are likely in phosphorus components of the nonliving, non-orthophosphate phosphorus pools. Secondly, those models generally do not address many of the current theories regarding controls of internal nutrient cycling. Only by including those theories (e.g., the effects of animal migration and patchiness in general, abiotic/biotic and phytoplankton/bacteria competition for nutrient ions, and sedimentary and resuspended material), can their significance in the larger ecosystem context be examined.

It is for these reasons that a conceptual model identifying many of the missing components and dynamics is proposed below.

CONCEPTUAL MODEL OF PHOSPHORUS CYCLING IN THE GREAT LAKES

This conceptualization is not intended to be implemented computationally in its entirety, but rather is an attempt to recognize potentially important aspects of the phosphorus cycle. Subsequent definitions of appropriate time and space scales and consideration of the physics will assist in identification of important and consistent (for those scales) components and processes.

The material that follows is based, in large part, on information drawn from the preceding chapters and represents a synthesis of the material reviewed and ideas proposed into a somewhat complete whole-system framework. This framework serves as a background against which the significance of individual components and processes can be judged.

Phosphorus Transport

Figure 1 is a representation of major physical and migratory processes that are superimposed all over biological and chemical in situ transformations. Boyce (1974) and Lick (1979) reviewed aspects of large- and small-scale circulation, vertical and horizontal dispersion, and waves and resuspension as they relate to biological and chemical properties and transport of contaminants. Vertical and horizontal migration of zooplankton, fish, and benthic animals can, at times, be significant modes of transport. This is particularly true when dominant physiological processes depend on position in the migratory patterns (see Bowers, Chapter IV). Sinking ensures a long-term net downward transport of particulate material. Experience has indicated that, for large, spatially (horizontal and vertical) averaged Great Lakes models, phytoplankton sinking is not a particularly important mass flux process on short time scales (<1 year). On longer time scales, sinking is the dominant process. Sinking of nonliving particulate material may be significant on both time scales. The significance is tied closely to the scavaging effect of sorption onto these particles.

All of these processes interact and impact on biological and chemical properties in lakes; their relative importance is keyed to time and space scales that are under investigation (see Harris 1980). To compare the influence of these transport phenomena to rates of in situ transformations, Table 1 was constructed. For processes like these, only the spatial scales of interest need be defined, for time scales are dictated by the process and space scale. In the first column in Table 1 maximum expected rates of transport are

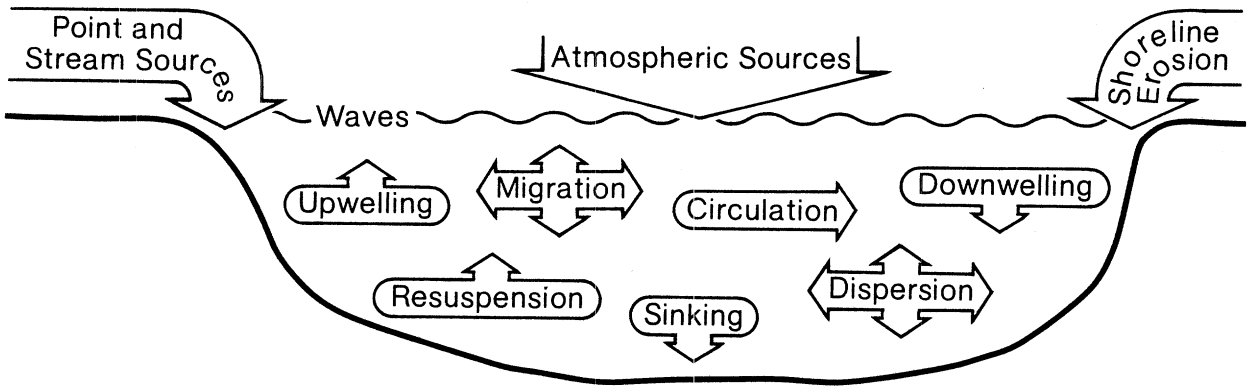


Fig. 1. Phosphorus sources and transport.

TABLE 1. Time constants for transportation phenomena.

	Maximum Transport Rates	Upper Limit Rate Constant
Upwelling	10 m day^{-1}	10 day^{-1}
Downwelling	10 m day^{-1}	10 day^{-1}
Large-scale circulation (horizontal)	10,000 m day^{-1}	10 day^{-1}
Small-scale circulation (vertical) (e.g., Langmuir)	1,000 m day^{-1}	1,000 day^{-1}
Migration: zoo (vertical)	100 m day^{-1}	100 day^{-1}
Migration: fish (horizontal)	10,000 m day^{-1}	10 day^{-1}
Sinking	10 m day^{-1}	10 day^{-1}
Dispersion: vertical	1 $m^2 day^{-1}$	1 day^{-1}
horizontal	$10^6 m^2 day^{-1}$	1 day^{-1}

Minimum vertical scale = 1 m
Minimum horizontal scale = 1000 m

given. Assuming minimal spatial scales of interest of 1 m (vertically) and 1 km (horizontally) then upper limit, reciprocal residence times (column 2) can be calculated. These time constants quantify the maximum effect of the transport processes on the given spatial scales and can be used to identify those processes that "compete" with biological and chemical processes (discussed below) on these scales. Other space scales can (and should) be considered. Also, these assumed space scales will not necessarily resolve all transport processes.

Phosphorus Components in the Water Column

At any particular location within the lake, many biological and chemical processes are acting simultaneously to transform phosphorus among its many chemical forms. A representation of those forms and probable important pathways of phosphorus flux in the Great Lakes are illustrated in Figure 2.

Living Components

The right half of the figure is dominated by living components including food web and fecal pathways among phytoplankton, bacteria, protozoa, rotifers, crustaceans, and fish. Although difficult to illustrate on the figure, some of the most important aspects of the control of phosphorus dynamics from the top of the food web are keyed to predatory effects on community structure. For example, given increasing metabolic rates with decreasing animal size, the size-dependent nature of fish predation on the zooplankton community becomes increasingly important (see Kitchell, Chapter V). To investigate these and similar effects, several functional groups and perhaps life-stage categories must be considered throughout the food web. Suggested criteria for separation of functional groups are included in Table 2.

Another property that has been included previously in some models, and apparently must be included, is internal pools of readily exchangeable phosphorus within bacteria and phytoplankton cells. While the kinetics of exchange among external, internal, and biomass pools of phosphorus must be considered carefully in the context of specified time scales, there is no question that the consequence of interaction among these pools - variable cell nutrient stoichiometry - must be included (see Lehman, Chapter IV).

Nonliving Components

The left half of Figure 2 represents the nonliving matrix of phosphorus components. Here truly soluble components exist "freely dissolved" or sorbed to particulate material. Sorption processes may serve to buffer the more transient processes by providing a reservoir of material. This reservoir is built up during periods of high concentration of dissolved material and subsequently released during periods of lower concentration.

Dissolved inorganic components of this nonliving matrix can be separated out easily on functional, if not analytical, grounds. For example, dissolved orthophosphate (PO_4) fills the special role of being the end product of most

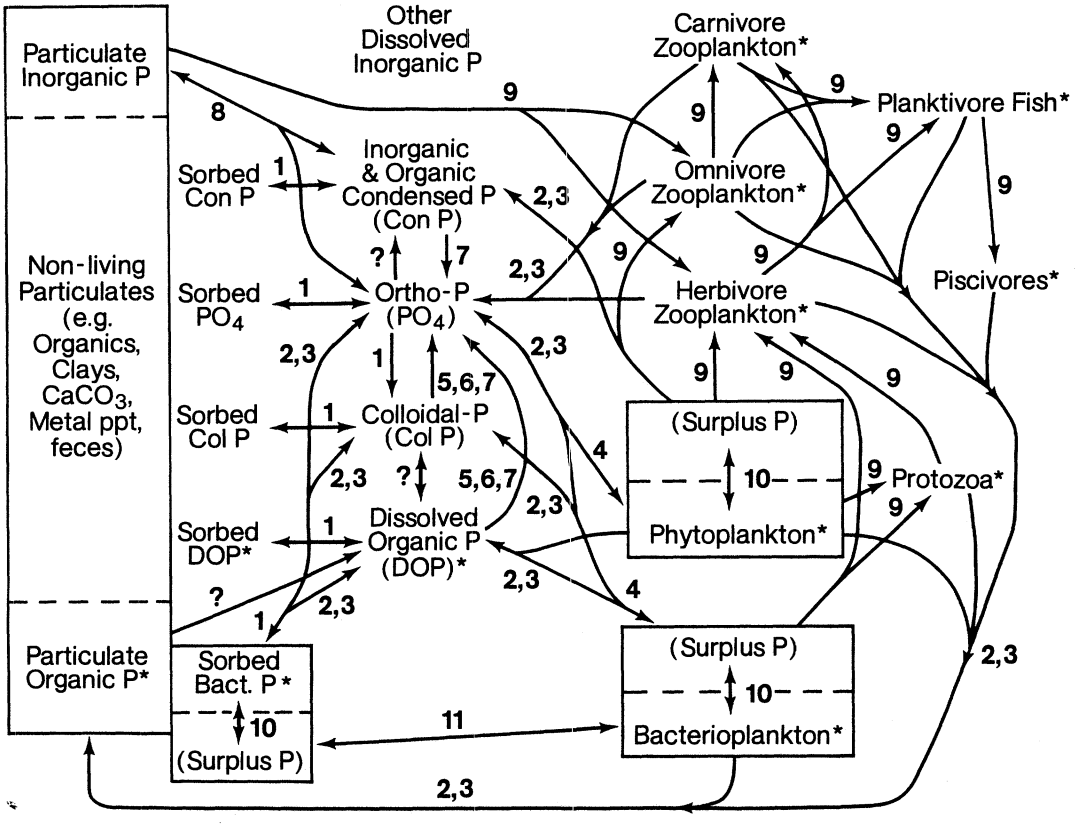


Fig. 2. Phosphorus flow diagram indicating major components and pathways within the water column. * indicates several functional groups or life stages within each component. Numbers represent processes identified in Table 4.

degradation processes, as well as being the only form of phosphorus immediately available for assimilation by algae. Although conventional analytical methods can only approximate the concentration of PO_4 (see Tarapchak, Chapter I; Gardner and Eadie, Chapter II), it is important to understand and attempt to describe the flux of phosphorus through this important pool. Inorganic condensed phosphates may or may not play an important role in the phosphorus cycle. These compounds (e.g., the polyphosphates) are the principal storage products of surplus phosphorus in algae, but their stability and importance outside the cell are not well known. This conceptualization (Figure 2) recognizes the potential importance of this group of compounds. A suite of other dissolved inorganic compounds (e.g., inorganic complexes) may also exist, although their relative abundance and importance are unknown.

Dissolved organic phosphorus compounds are probably the least well understood group. Condensed organic phosphates (e.g., ATP, ADP) are key compounds in metabolic and energetic processes within organisms, but their relative stability and importance as compounds outside organisms are not clearly understood. Organic compounds, other than these condensed forms, fall into a mesh of overlapping categories (e.g., humic acids, organic complexes, phytic acids, nucleotides). The role of this group, or more accurately the

TABLE 2. Criteria for disaggregation of functional groups.

Particulate Organics (+ other particulates)
-- size
-- lability
-- sorption capacity
Dissolved Phosphorus
-- inorganic/organic
-- lability
-- sorption characteristics
Bacteria
-- food sources
-- planktonic
-- "attached"
Phytoplankton
-- size
-- resource requirements (Si, P, N)
-- kinetic response capability
Zooplankton
-- size
-- food selection
-- kinetic response capability
-- life history
Fish
-- food selection
-- life history

roles of components within this group, has not been studied extensively. At this stage only speculation can be used to identify the important components. Perhaps the best approach to conceptualize important components is to visualize the compounds on a "degradability" or "labile-refractory" continuum, which may or may not be related to component size (or molecular weight). This is discussed further below with particulate organic P.

The colloidal pool is identified on Figure 2 to emphasize the fact that this pool (mainly a size-dependent definition) can be important. Because this pool is defined only by size characteristics, its functional characteristics include a wide spectrum of processes and attributes (both inorganic and organic) and it therefore requires the same scrutiny relating to lability as the truly dissolved components.

Particulate components of the nonliving pool generally can be divided into inorganic and organic classes, although organic coatings on inorganic particles and inorganic "intrusions" (e.g., silica frustules in fecal pellets) make even

this distinction difficult. The role of particulates falls into two categories in terms of controls of phosphorus cycling: 1) a site for sorption of dissolved components, 2) a source or sink for dissolved components from phosphorus incorporated into the particulate material. Examples of the sorption role are sorption onto $CaCO_3$ particles, clays, and metal precipitates [e.g. $Fe(OH)_3$]. Particulate inorganic phosphorus compounds are generally considered to be not important in the water column. Examples of the second role are phosphorus compounds found in dead algae fragments and zooplankton fecal material. Algal fragments and fecal material can also serve as sorption sites.

Like the dissolved components, particulate organic phosphorus components represent spectra of size and lability. Although particulate and dissolved components are represented on Figure 2 in discrete classes, Figure 3 better represents this nonliving matrix. Entries in the matrix represent only what can be implied from the paucity of available information: that a large fraction of naturally occurring phosphorus compounds in this nonliving matrix must be classified presently as amorphous, and that the limits of lability indicated on Figure 3 for many of the constituents are not well known. As more information becomes available to fill out the matrix, not only may logical functional groups of compounds be identified, but also potential classification of constituents in water samples of unknown composition may be possible.

Typical Pool Sizes

Table 3 lists typical summer pool sizes. For many of the components (e.g. condensed P, colloidal P, protozoa) very little or no information is available for the Great Lakes. Even where data are available, they are general and crude. Orthophosphorus is probably less than 0.1 $\mu g\ P\ L^{-1}$ in many lakes since SRP measurements (likely an overestimate; see Tarapchak, Chapter I) in Lake Ontario, for example, are ca. 1.0 $\mu g\ P\ L^{-1}$. SUP, which estimates the nonliving matrix (Figure 3) in the less-than-0.45 μm size range, in Lake Ontario is typically on the order of 10 $\mu g\ P\ L^{-1}$. Phytoplankton P, estimated from direct counts, carbon per cell, and Redfield's ratio, is ca. 5 $\mu g\ P\ L^{-1}$ in Lake Ontario. The nonliving >0.45 μm size range (PP), approximated by total P (TP=25 $\mu g\ P\ L^{-1}$) - total dissolved P(TDP) - phytoplankton P, contains about 10 $\mu g\ P\ L^{-1}$ in Lake Ontario. Phytoplankton and detrital organic carbon concentrations are comparable in the summer epilimnion of Lake Ontario. Assuming (as a maximum for detritus) the same is true in terms of phosphorus, TP-TDP-phytoplankton P-Detrital P = 5 $\mu g\ P\ L^{-1}$ provides an estimate of phosphorus associated with inorganic particles, leaving 5 $\mu g\ P\ L^{-1}$ associated with organics. Since little epilimnetic P is truly particulate inorganic, the former component is likely to be phosphorus sorbed to inorganic particles.

Phosphorus concentrations associated with herbivorous, omnivorous, and carnivorous crustaceans, approximated by simulation and by dry weight observations converted stoichiometrically, are typically 1.0, 1.0, and 0.1 $\mu g\ P\ L^{-1}$, respectively (see Scavia 1980). Rotifer concentrations in nearshore Lake Ontario are on the order of 1000-1500 ind L^{-1} (McNaught *et al.* 1973). Using dry weight estimates from Nalepa (1972) and a phosphorus content of about 1%, rotifer phosphorus may be ca. 0.1 $\mu g\ P\ L^{-1}$.

Bacterioplankton typically number 10^6 cells mL^{-1} in lakes and oceans (e.g. Wiebe and Pomeroy 1972), and one study (Barsdate *et al.* 1974) of a tundra pond

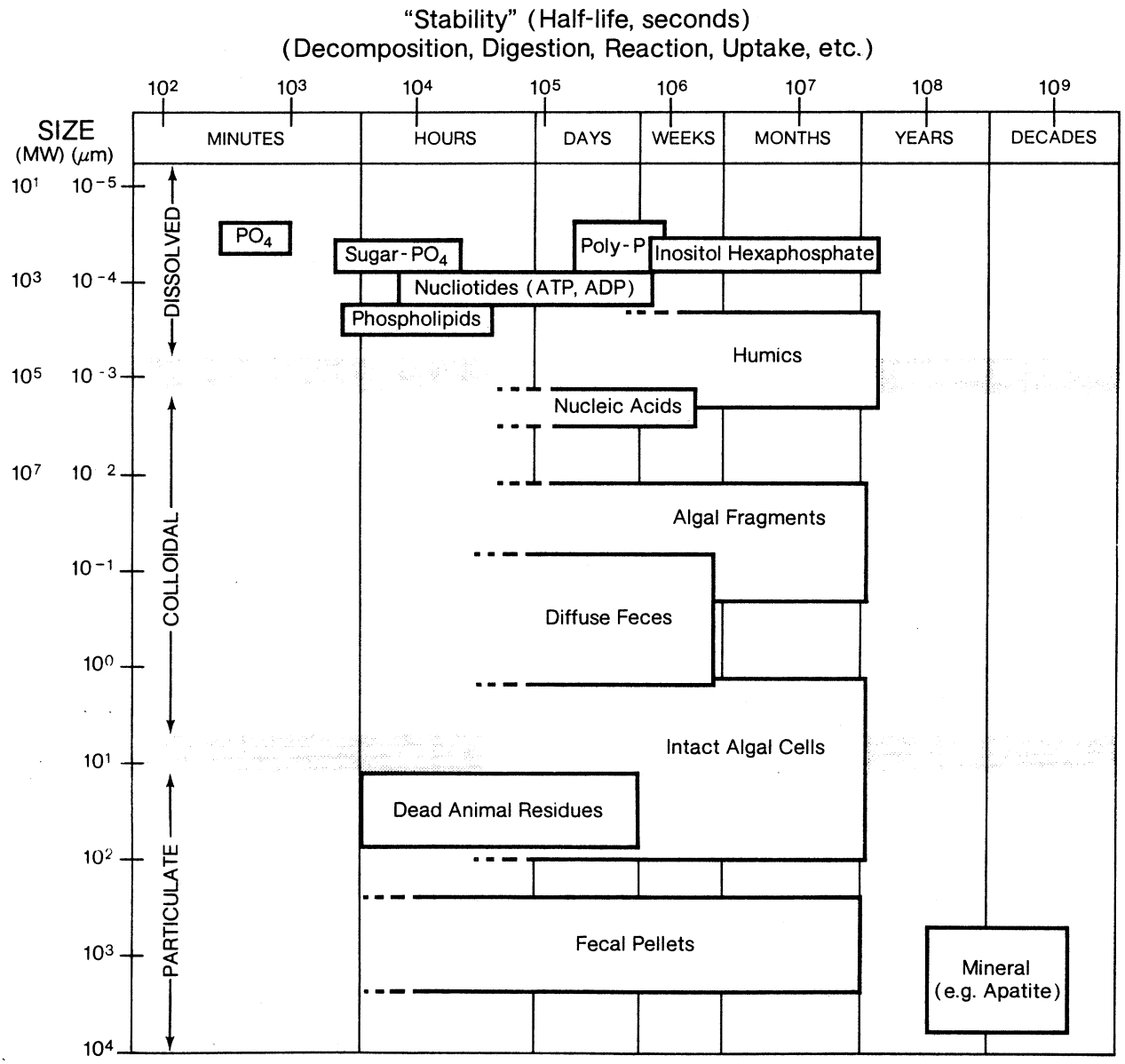


Fig. 3. Size-stability matrix of nonliving phosphorus components indicating approximate location of identifiable fractions.

ecosytem measured 2.6×10^{-9} μg P $cell^{-1}$ for bacteria. These numbers indicate a possibility of ca. 2.6 μg P L^{-1} due to bacteria alone. Concentrations of bacteria attached to particles are perhaps one-tenth of free swimming bacteria (see Moll and Brahce, Chapter III).

In Situ Transformations

Important phosphorus components are illustrated in Figures 2 and 3 and typical pool sizes are listed in Table 3. Important processes contributing to transport of those components are illustrated in Figure 1 and typical rates are

TABLE 3. Typical pool sizes.

Pool	Concentration ($\mu g\ P\ L^{-1}$)
Dissolved orthophosphate (<SRP)	<0.1
Nonliving (<.45 μm, SUP)	10.0
Nonliving (>.45 μm, organic)	5.0
Sorbed to Inorganic Particles	5.0
Bacterioplankton	1.0-10.0
Attached Bacteria	0.1-1.0
Phytoplankton	5.0
Herbivore crustaceans	1.0
Omnivore crustaceans	1.0
Carnivore crustaceans	0.1
Rotifers	0.1
Planktivore fish	0.01-1.0
Piscivore fish	0.001-0.1
Total P	25

listed in Table 1. Important biological and chemical processes that cause transformations of the components resulting in fluxes among the boxes in Figure 2 and, in effect competing with the processes listed on Table 1, are illustrated as numbered arrows on Figure 2. The processes are listed by those numbers in Table 4 where typical, phosphorus-specific rate constants are given. These rates are by no means a synthesis of all existing information. They represent typical ranges of values accumulated through a cursory investigation of the literature. These rate constants multiplied by the expected pool sizes (Table 3) indicate approximate fluxes among the compartments.

Examination of fluxes presents a crude approximation of the relative importance of various process/pool interactions in controlling the cycling of phosphorus. It also illustrates relative time scales of consideration for processes. For example, on a 1-day time scale bacterial uptake may appear always in equilibrium with external P concentrations, whereas animal nonpredatory death may appear not to occur at all.

Simultaneous consideration of physical, biological, and chemical processes affecting the phosphorus cycling will require careful matching and selection of time and space scales. Biological and chemical processes synthesized into general categories (Table 5) should be compared with the transportation process rates in the second column of Table 1. The rate constants are compared graphically, assuming minimum transport space scales of 1 m vertically and 1 km

TABLE 4. Detailed rate constants and estimates of flux.

No.	Process	Rate Constant (day^{-1})	Pool Size ($\mu gP\ L^{-1}$)	Flux ($\mu gP\ L^{-1} day^{-1}$)
(1)	Sorption			
	PO_4 to seston	10	<.1	<1.0
	PO_4 to Hydroxides	100	<.1	<10
(2)	Death			
	Bacteria	.001	1-10	.001-.01
	Phytoplankton	.01-.1	1-10	.01-1.0
	Herbivore crustaceans	.01	1.0	.01
	Omnivore crustaceans	.01	1.0	.01
	Carnivore crustaceans	.01	.1	.001
	Planktivore fish	.01	.01-.1	.0001-.001
	Piscavore fish	.01	.001-.01	.00001-.0001
	Rotifers	.01	0.1	.001
	Protozoa	.01	?	?
(3)	Excretion/Egestion			
	Bacteria	10	1-10	10-100
	Phyto (to DOP)	0.1	1-10	0.1-1.0
	Herbivore crustaceans (to PO_4)	.001-10.	1.0	.001-10.0
	Omnivore crustaceans (to PO_4)	.001-1.0	1.0	.001-1.0
	Carnivore crustaceans (to PO_4)	.001-1.0	0.1	.0001-.1
	Rotifers	?	?	?
	Planktivore fish	.001	.01-.1	$.10^{-5}$-10^{-4}
	Piscavore fish	.001	.001-.01	10^{-6}-10^{-5}
	Protozoa	?	?	?
	"Decay"			
	ORG - Inorg	.01	15(POP+DOP)	.15
(4)	Uptake			
	Phytoplankton	10	1-10	10-100
	Bacteria	100	1-10	100-1000
(5)	Enzymatic release (alk. phos. on DOP)	0.1-1.0	10	1-10
(6)	Photolysis (of DOP)	1-10	10	10-100
(7)	Hydrolysis			
	of Cond P	.01-.1	?	?
	of org P	1-10	10	1000

(continued).

TABLE 4. (continued).

No.	Process	Rate Constant (day^{-1})	Pool Size ($\mu gP\ L^{-1}$)	Flux ($\mu gP\ L^{-1} day^{-1}$)
(9)	Feeding			
	Protozoa	?	?	?
	Herbivore crustaceans	0.1-1.0	1.0	.1-1.0
	Omnivore crustaceans	0.1-1.0	1.0	.1-1.0
	Carnivore crustaceans	0.1-1.0	0.1	.01-.1
	Planktivore fish	0.01-0.1	.01-.1	.0001-.01
	Piscavore fish	0.01-0.1	.001-.01	.00001-.001
	Rotifers	0.1-1.	0.1	.01-.1
(10)	Growth			
	Phytoplankton (on internal P)	1	1-10	1-10
	Bacteria (on internal P)	10	1-10	10-100

TABLE 5. List of general biological and chemical processes.

No.	Process	Rate Constant (day^{-1})
1	Sorption	10^1-10^2
2	Death	10^{-3}-10^{-1}
3	Excretion/egestion	10^{-3}-10^1
4	Uptake	10^1-10^2
5	Enzymatic release	10^{-1}-10^0
6	Photolysis	10^0-10^1
7	Hydrolysis	10^{-2}-10^1
8	Precipitation reactions	?
9	Feeding	10^{-2}-10^0
10	Growth (on internal P)	10^0-10^1
11	Microbial colonization	?

horizontally, in Figure 4. From this display it becomes clear that careful attention must be given to the interactions of physical, biological, and chemical processes on varying time and space scales. This is true for both modeling and experimental considerations (see Harris 1980).

Sediment/Water Interface

To this point only processes and components affecting phosphorus cycling in the water column have been discussed. Transport across the sediment/water interface, also an important process, is affected by many properties and processes interacting within the sediment. The most important factors are identified in Figure 5.

The sediment region is composed of particulate material, pore water contituents, and permanent and migratory organisms. Transformation of phosphorus species, translocation within the sediment, and translocation into and out of the sediment are processes labeled on Figure 5 and identified in Table 6. Along with each process or property in Table 6 is a suggested list of functions controlling that process and, where available, estimates of flux rates. Presently, the qualitative controls of phosphorus exchange are beginning to emerge, however very little is known of the quantitative and mechanistic nature of these controls.

DISCUSSION

The material in this chapter represents a synthesis of information from the previous chapters as well as other literature sources. An attempt is made to outline important components (Figures 2 and 5) of the phosphorus cycle and

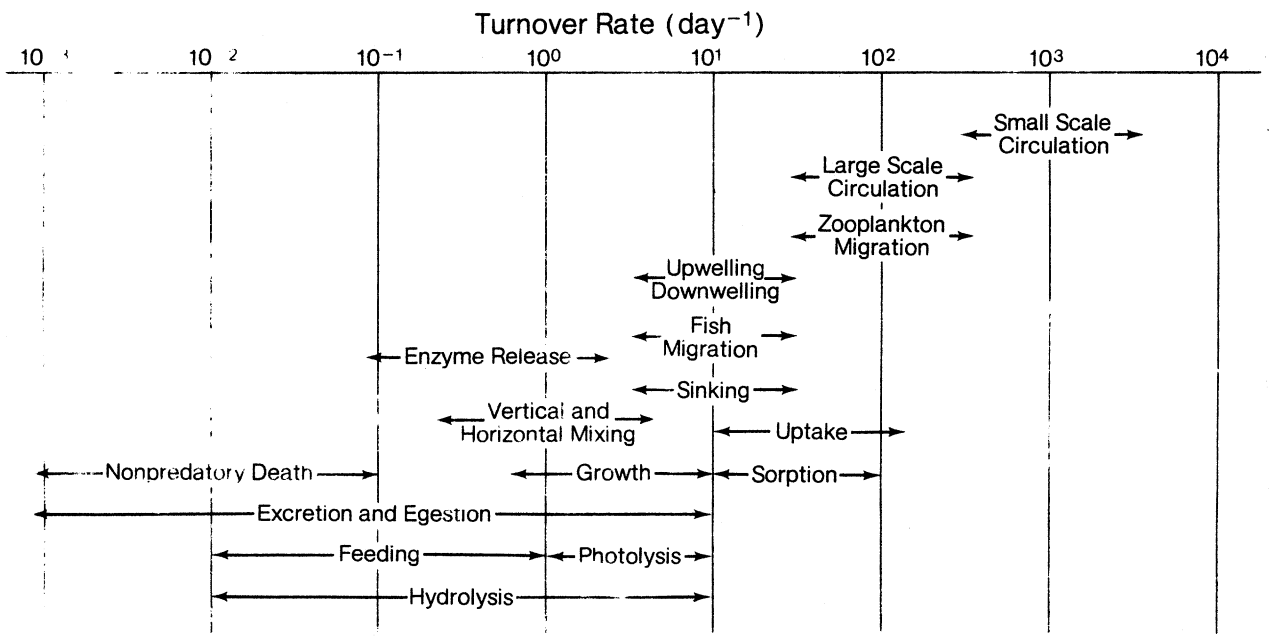


Fig. 4. Comparison of physical and biological/chemical process time scales. Physical processes assumed important on 1 m vertical and 1 km horizontal space scales.

TABLE 6. Processes at the sediment-water interface.

No.	Processes	Rates	Flux
1	Deposition (particle size, composition)		10^{-4}-10^{-3} gPm^{-2} day^{-1}
2	Resuspension (waves; currents; reworked, uncompacted sediments from processes (4) and (5))		
3	Animal migration (translocated processes; meiofauna)	10^{0}-10^{1} m hr^{-1}	
4	Pontoporeia ("eddy-diffusers" of particulates; see (2))		
5	Tubificids (conveyor transport of solids and water from 2-5 cm to top; see (3))		
6	Chironomids (water pumpers mainly, from 2-5 cm)		
7	Pore water and interface diffusion	10^{-5}-10^{-6} m^{2} day^{-1}	10^{-2}-10^{-1} gPm^{-2} day^{-1}
8	Particulate - pore water exchange (many processes similar to heterotrophic water column; chemical equilibrium - sorption; biological egestion excretion, feeding macro-, meio-, micro-benthos)	See Figure 3 and Table 4	

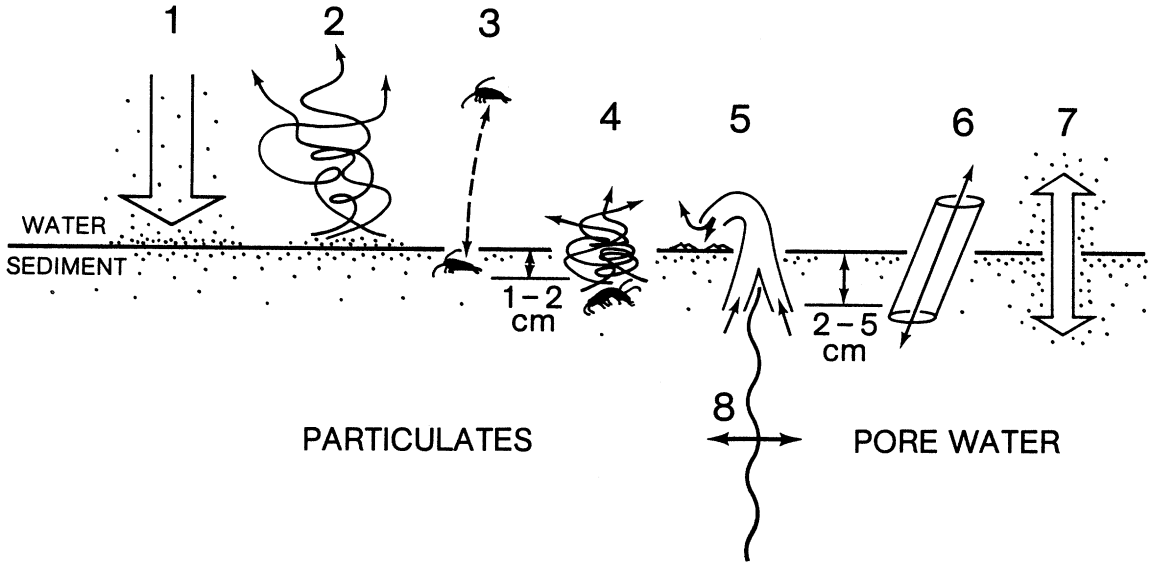


Fig. 5. Conceptualization of major processes acting at the sediment-water interface. Numbers represent processes identified in Table 6.

to suggest a logical basis (Figure 3) for identifying other important components, especially within nonliving phosphorus pools. Pool sizes typical for the Great Lakes (especially Lake Ontario) are given (Table 3) for components where data are available.

Important pathways of phosphorus flows among components are indicated (Figures 2 and 5) and flux estimates are given (Tables 4, 5, and 6). Although the flux estimates are crude, they can be useful for examining the relative importance of the pathways. The true impact of each pathway also is determined somewhat by time scales under consideration. While the pathways are quantified somewhat by examining ranges of flux rates, no attempt was made to describe any controls of processes identified as pathways. The next step in development of pertinent information on phosphorus cycling will be to define and refine equations that approximate those processes and their functional controls.

These transformation processes are often considered intrinsic properties when viewed in light of water transport, i.e., reactions within a parcel of water are not affected by the dimension of that parcel. This is only true, however, for a homogeneous environment. Harris (1980) discusses some important consequences of ignoring spatial heterogeneity in phytoplankton populations. It appears that averaging a specific process (say phytoplankton uptake) over a space scale several times the size of a phytoplankton patch will result in a rate quite different from one within the patch. Consequently, measurement and simulation of biological and chemical processes may be space-scale dependent and therefore tied intimately to transport processes.

Some important transport processes are illustrated in Figure 1 and typical rates identified in Table 1. Assuming minimum spatial scales of 1 m vertically and 1 km horizontally (the scales at which much of the presently available biological and chemical rate information is pertinent) the effects of transport versus in situ transformation are compared in Figure 4. It is through consideration of both transformation and transport processes at proper time and space scales that the relative importance of the processes will emerge.

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